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Catalytic Destruction of Monochloramine Using Granular Activated Carbon for Point of Use Applications

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Catalytic Destruction of Monochloramine Using Granular Activated Carbon for Point of Use Applications

by

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Thesis

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Dedication

In loving memory of my father, Charles, who passed away during my time at the University of Texas. Also, to my mother, Kathleen, for remaining strong throughout the hard times and always pushing me to succeed.

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Abstract

Catalytic Destruction of Monochloramine Using Granular Activated Carbon for Point of Use Applications

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The University of Texas at Austin, 2013

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Chloramines are used for disinfection in many water treatment facilities because of their ability to provide residual protection of water supplies while minimizing the formation of disinfection-by-products. However, chloramines can impart taste and odor to the water, which can lead to customer complaints. Furthermore, the removal of monochloramine from water is essential for certain industries. Previous research at the University of Texas at Austin has demonstrated the potential of several granular activated carbons (GAC) for removal of monochloramine under conditions typical of water treatment plants. The goal of this research project is to further quantify steady-state monochloramine reduction in fixed bed reactors (FBR) with three commercially available GACs, and improve the understanding of the physical and chemical properties that influence removal. The research was divided into 3 phases:

1. A laboratory scale fixed bed reactor experiment was used to quantify steady state monochloramine removal over time. City of Austin tap water

was used for three GAC types (Jacobi CAT, Norit CAT, Nority CNS) at pH 8 and 9.

2. Physical characterization of each GAC was performed using analysis of nitrogen adsorption isotherms. Specific surface area, pore volume, and pore distribution were determined. Chemical characterization was performed quantitatively using Boehm titrations. Qualitative analysis was performed by analyzing FTIR spectra of untreated activated carbon samples.
3. The Monochloramine Catalysis (MCAT) model was calibrated using results from the Phase 1 and 2 experiments. Simulations of full scale point of use drinking water filters were run for various empty bed contact times and influent monochloramine concentrations. These results were compared against National Sanitation Foundation monochloramine reduction certification criteria.

Results show that steady state removal was achieved for all of the activated carbons tested and this removal efficiency can reach nearly 90% using a 0.75-minute empty bed contact time. This steady state performance indicated that catalysis of the monochloramine was occurring, and removal could theoretically occur for very long periods of time. The second stage of the research shows correlation between chemical characteristics (acidity and basicity) and removal efficiency. Furthermore, physical characteristics, mainly micro-porosity, were shown to largely impact performance. Finally, the MCAT model provides a reasonable estimate of steady state removal, and is used to predict full scale point of use performance.

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Chapter 1: Introduction

1.1. Research Motivation

Monochloramines are generally used as a secondary disinfectant in many water treatment facilities, as an alternative to chlorination. In the recent years, knowledge of disinfection by products (DBPs) has sparked a surge in interest to chloramination. Although monochloramine does have a tendency to produce DBPs, by-product formation is much lower with monochloramine than with traditional free chlorine. In fact, chloramination reduces DBP formation by 40 to 80 % (American Water Works, 2004). Additionally, waters that are treated with chloramines do not generally emit the distinct chlorine odor associated with traditional methods (Environmental Protection Agency, 1999). Monochloramine does lack the raw disinfection power that free chlorine does. Therefore, it is typically not used as a primary disinfectant. However, chloramines do provide a longer residual disinfectant, where the unstable free chlorine reacts quickly.

Although monochloramine has many advantages, consumption in certain forms can be dangerous. Monochloramine cannot be present for the production of water for kidney dialysis, soft drink manufacturing, and fishery operations (Komorita & Snoeyink, 1985). Research by Snoeyink and co-workers demonstrated the catalytic properties of activated carbon for destruction of monochloramine (Kim, 1977; Komorita & Snoeyink, 1985). Fairey et al. (2006) conducted in-depth analysis of various granular activated carbons (GACs) for monochloramine removal in fixed bed reactors. This research is an extension of the work of Fairey et al. to assess the feasibility of advanced GACs for the removal of monochloramine in point of use water filters, where taste complaints make monochloramine in drinking water undesirable. It is intended that results from this research will not only identify which of the three GACs tested is more suitable for use in

point of use filtration systems, but will also confirm relationships between various physical and chemical characteristics and fixed bed reactor performance that were identified by Fairey et al. (2006). Ideally, a summary of results would show optimal characteristics, so future GACs can be tailored to perform more efficiently, without the need for expensive trial and error pilot tests.

1.2. BACKGROUND INFORMATION

The reduction of free chlorine and/or chloramines has been studied at length (Bauer & Snoeyink, 1973; Kim, 1977; Suidan et al., 1977a; Suidan et al., 1977b; Kim et al., 1978a; Kim et al., 1978b; Kim & Snoeyink, 1980a; Kim & Snoeyink, 1980b; Komorita & Snoeyink, 1985; Voudrias et al., 1985). In 1977, Kim's research showed that monochloramine reactions with GAC in fixed-bed reactors (FBRs) reached a steady-state following a period of higher removal for a given set of influent conditions, namely: monochloramine influent concentration, activated carbon particle size, and empty bed contact time (EBCT). When applied to engineering applications, these results indicate that the GAC would not require regeneration or replacement, as long as the steady-state effluent concentration satisfactorily met removal goals. Kim (1977) also created a finite element model that assumed pore diffusion as the rate limiting mechanism. This model was calibrated for Kim's experiments and served as a means to estimate steady-state effluent monochloramine concentrations for full scale columns.

Komorita and Snoeyink (1985) utilized this model as a springboard to investigate steady-state monochloramine removal. After combining FBR results with modeling exercises, their results showed impractically large EBCTs would be needed to conform to the kidney dialysis standard of 0.1 mg/L as Cl_2. However, in recent years, GACs have

been developed with enhanced catalytic properties. The major methodology for introducing higher catalytic activity to the surface of the carbon particle was developed and refined by Chou (1986) and Matviya and Hayden (1994). In 2006, Fairey et al. conducted rigorous studies as a means to bridge this research gap. Two catalytic GACs, Calgon Centaur and MeadWestvaco Aquaguard were compared in various studies with traditional activated carbons. Fairey et al. (2006) showed that modified GACs did have the potential to achieve much higher steady-state removal. Furthermore, physical and chemical properties of the activated carbon were shown to correlate to catalytic removal efficiency. Finally, the impact of water characteristics, mainly pH and the presence of natural organic matter (NOM), were quantified and shown to impact monochloramine reduction to varying, but significant degrees. This research was proposed to further assess catalytic monochloramine removal, but in point of use applications. Three commercially available GACs were compared to provide stronger understanding of the processes involved in the catalysis reaction of monochloramine with activated carbon.

1.3. RESEARCH OBJECTIVES

The objectives of this research were to (1) quantify steady-state monochloramine reduction in fixed bed reactors (FBRs) by the GAC type and source water characteristics, (2) improve understanding of physical and chemical properties that influence removal so GAC characteristics can be further optimized, and (3) model full-scale performance with regards to steady state monochloramine reduction so that the feasibility of point of use applications can be assessed.

1.4. RESEARCH APPROACH

The three research objectives were evaluated with the following three phases of the project:

1. Steady-state monochloramine reduction in laboratory scale fixed bed reactors was quantified for three commercially available granular activated carbons (Jacobi CAT, Norit CAT, Norit CNS) using City of Austin tap water as the representative source water for point of use applications.

2. Physical properties of the activated carbons such as specific surface area, pore volume, pore size distribution were quantified. Chemical properties such as the nature of surface functional groups, electrostatic properties, and acidity/basicity were characterized. The results from the analysis of physical and chemical properties were compared to results from Phase 1 in an attempt to correlate performance with surface properties. Thus, the properties that influenced monochloramine reduction could be elucidated.

3. The numerical monochloramine catalysis model developed by Kim in 1977 was calibrated using the steady state results from laboratory scale experiments run in Phase 1. Certain physical characteristics determined in Phase 2 were incorporated as modeling parameters. Model simulations were run for GAC particle sizes used in practice under various conditions. Results were used to assess the feasibility of using these activated carbons for point of use removal of monochloramine from treated drinking water.

1.5. REPORT STRUCTURE

This report is divided into five chapters, introduction, literature review, materials and methods, results and discussion, and conclusions. Chapter 1 provides a brief introduction of the research, along with the motivations and objectives associated with the project. Chapter 2 provides a more in-depth presentation of background information needed for this research. It presents monochloramine chemistry, as well as the principles of activated carbon when applied to water treatment. Chapter 3 presents the materials and methodology that were utilized in this research. The experimental and modeling results are presented and analyzed in Chapter 4. Finally, Chapter 5 contains conclusions that are relevant to the project and point of use applications; additionally, recommendations for future work are highlighted.

Chapter 2: Literature Review

2.1. OVERVIEW

Literature that represents current scientific understanding of monochloramine and granular activated carbon is presented in this chapter. The following information is pertinent to the project and was used to develop experiments and/or analyze results. Background knowledge offered includes monochloramine chemistry, reactions of activated carbon with monochloramine, activated carbon physical properties, surface chemistry properties, and the numerical modeling of monochloramine reduction with GAC using the methodology of Kim (1977).

Previous work at the University of Texas investigated various GAC's ability to catalytically destroy monochloramine (Fairey et al., 2006). Thus, various pertinent experimental conditions had been evaluated and were incorporated into this research. Modifications of this experimental setup were created to mimic point of use applications. To perform the FBR study, a monochloramine concentration influent was required at a stable pH between 7 and 9, which is the normal range for chloramination. Monochloramine formation and behavior based on traditional operating parameters, such as chlorine to nitrogen (Cl_2:N) ratio and pH are discussed, and a review of the monochloramine reactions associated with GAC surfaces is provided. Pertinent hydrodynamic parameters used in previous FBR studies are also given to provide a basis for the experimental design used in this research. An explanation of certain relevant physical and chemical properties used to evaluate activated carbon samples are also introduced for comprehension of results presented in following chapters. Finally, details of the pore diffusion/surface catalysis model developed by Kim and Snoeyink and

incorporated into this research are presented to understand the capabilities and limitations of the model.

The main hypothesis of this research is that the physical and chemical properties of an activated carbon sample can be used to qualitatively predict monochloramine removal efficiency.

2.2. MONOCHLORAMINE CHEMISTRY

2.2.1. Introduction to Monochloramine

Chloramines are derivatives of ammonia where one, two, or three of the hydrogen atoms are substituted with chlorine atoms. The ammonia (NH_3) acts as a nucleophile that attacks the hypochlorous acid compound (HOCl) and strips the chlorine atom. The chemical formula of monochloramine is NH_2Cl. As further chlorination of the parent ammonia atom occurs, dichloramine ($NHCl_2$) and trichloramine ($NHCl_3$) are formed.

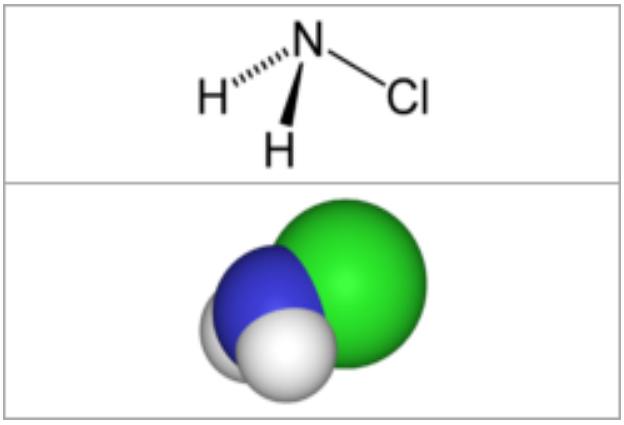

Figure 2-1. Representation and schematic of monochloramine.

As monochloramine destruction is the sole focus of this research, selected physical and chemical properties are depicted in Table 2-1 and a representation and schematic of monochloramine is shown below in Figure 2-1.

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Table 2-1. Physical and chemical properties of monochloramine.

Property	Comment
Molecular Formula	NH_2Cl
Appearance	Yellow Liquid
Melting Point	-66 °C, 207 K, -87 °F
Molar Mass	51.476 g/mol
Solubility in Water	Highly Soluble

Previous work has utilized ChemSketch software version 5.12 to calculate the molecular dimensions of monochloramine (Fairey et al., 2006). Based on this work, the molecule is approximately 5.3 Å long, 4.0 Å wide, and 3.6 Å deep. The dimensioned figure resulting from the software is presented in Figure 2-2 adapted from Fairey et al. (2006).

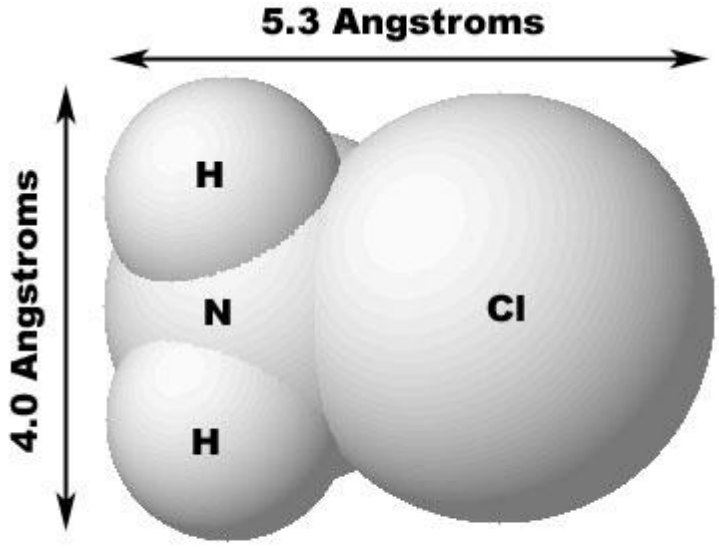


Figure 2-2. Molecular schematic of monochloramine using ChemSketch version 5.12.

2.2.2. Formation of Monochloramine

The formation of chloramines in water has been studied in great depth over the past years, as the use of chloramines as a secondary disinfectant has been rising. The formation and speciation of chloramines is summarized by the three step reaction mechanism shown below in equations 2-1 through 2-3. Hypochlorous acid (HOCl) and hypochlorite ion (OCl-) (note: together, these species are known as "free chlorine") react with ammonia (NH_3) or ammonium ion (NH_4^+) in a stepwise fashion (Bauer & Snoeyink, 1973):

$$NH_3 + HOCl = NH_2Cl + H_2O \text{ or } NH_4^+ + HOCl = NH_2Cl + H_2O + H^+ \quad (2\text{-}1)$$

$$NH_2Cl + HOCl = NHCl_2 + H_2O \quad (2\text{-}2)$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \quad (2\text{-}3)$$

The products of these reactions are monochloramine, dichloramine, and trichloramine. Dichloramine and trichloramine are undesirable with regards to drinking water treatment, as they have been shown to impart foul taste and odor complaints in the

water, and are even moderately toxic at concentrations above 0.8 and 0.2 mg/L as Cl_2, respectively (Wolfe et al., 1984). However, this is usually not a concern in waters of interest. Typical drinking waters range in pH from 7-9. Pressley et al. (1972) showed that monochloramine is the dominant species at pH values greater than 7, while dichloramine becomes dominant between pH 4.5 to 5, and trichloramine is only dominant in very acidic waters, with pH below 4.

Clearly, the speciation of chloramines is controlled by pH; however, another parameter, the Cl_2:N, dramatically affects the distribution of free chlorine, ammonia, and chloramines in a water system. At an appropriately high chlorine dosage, ammonia is completely oxidized to nitrate and nitrogen gas. This point is denoted in literature as the "breakpoint" and is the amount of chlorine that must be added before a free chlorine (HOCl + OCl-) residual is observed (American Water Works, 1999). This parameter is crucial in water treatment facilities during disinfection, as free chlorine is typically used as the primary disinfectant. Utilizing chemical equations and stoichiometry, the theoretical Cl_2:N mass ratio at the breakpoint is 7.6:1. In practice, this value is almost always higher, as reduced inorganic and organic species in the water are also oxidized by the chlorine. The American Water Works Association (1999) reports mass ratios approaching 15. The interaction of free chlorine, chloramine, and ammonia is best expressed graphically, with a typical breakpoint chlorination curve shown in Figure 2-3.

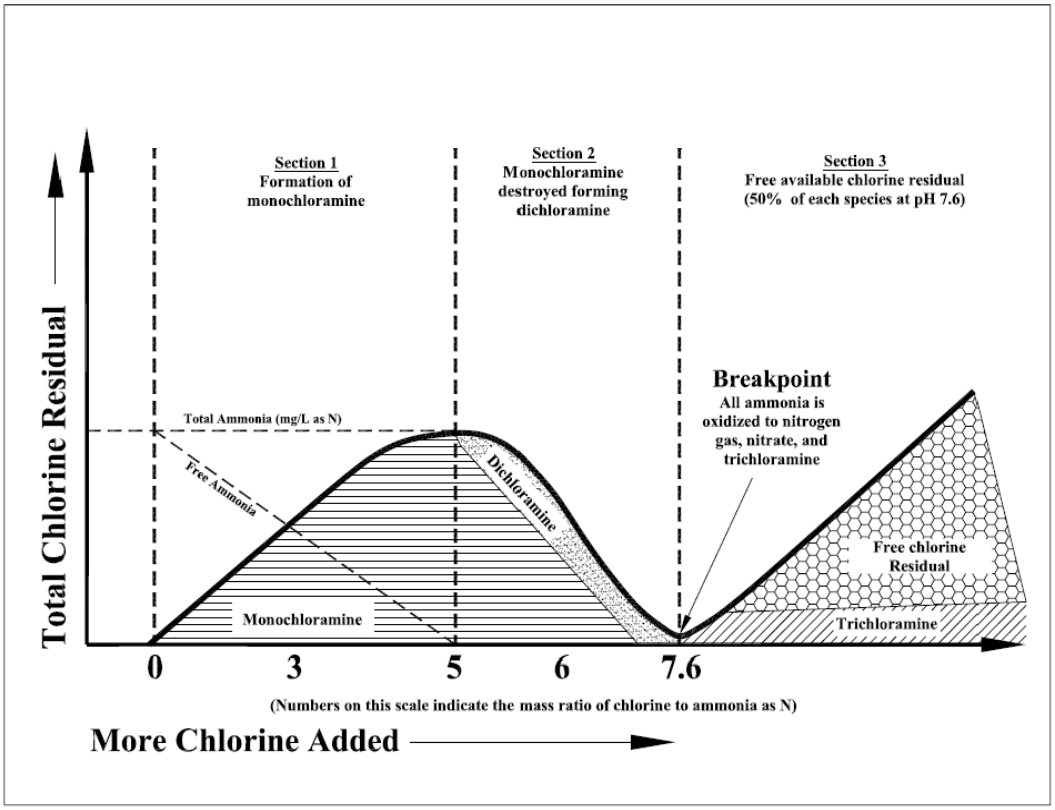


Figure 2-3. Typical breakthrough chlorination curve (adapted from Fairey et al., 2006).

Moving along the x axis of the figure can be envisioned as adding more free chlorine while holding the ammonia concentration higher. From the figure, it can be seen that water districts that utilize monochloramine for disinfection purposes would like to remain in a Cl_2:N ratio of between 3 and 5, as it is the region in which stable monochloramine formation occurs. A mass ratio of 5 is at the inflection point of the curve, and is typically avoided due to the impending formation of dichloramine that could result from minor errors. Typical utilities aim for a Cl_2:N ratio of 4 (American Water Works Association, 1999). The FBR experiments in this research utilized tap water as influent, so this mass ratio of 4 is expected.

2.3. ACTIVATED CARBON

2.3.1. Introduction

Activated carbon is a form of carbonaceous particle or granule that has been specially treated to make it extremely porous. (Marsh et al., 2006). It is used for the purification of water and air, and separation of gas mixtures. Activation is the selective gasification of carbon atoms through thermal activation. Typically, a high pressure steam is applied to the base carbon material, called the char. In recent years, "catalytic" activated carbons have been created that have additional surface functional groups that participate in chemical reactions. Activation of catalytic carbons is usually performed with an applied ammonia containing gas. Activated carbons are typically made from hard woods, coconut shell, fruit stones, coals, and synthetic macromolecular systems (Marsh et al., 2006). Because of the variety of base char materials, activation gas identity, and temperature applied, numerous GACs can be created that vary with respect to physical and chemical characteristics. To date, there are several hundreds of commercially available activated carbons, with different sizes of porosity, each targeted at specific applications.

2.3.2. Physical Properties of Activated Carbon

Activated carbons are often characterized by their specific surface area, pore size distribution, and pore volume. Due to the activation process, GACs can have a specific surface area (area contained per gram of carbon) from 500 to over 1500 m^2/g. In addition to raw surface area, the pore distribution of an activated carbon dramatically affects the number of surface sites that are accessible for adsorption due to competition with natural organic matter; in the case of this research, catalysis is performed in certain sites. Each of these three physical parameters can be determined through the analysis of adsorption

isotherms. An adsorption isotherm is a graphical representation of the relationship between the bulk activity of adsorbate (material to be adsorbed) at constant temperature to the adsorbed phase concentration (Stumm and Morgan, 1981). Figure 2-4 depicts the six adsorption isotherms that are commonly seen in practice.

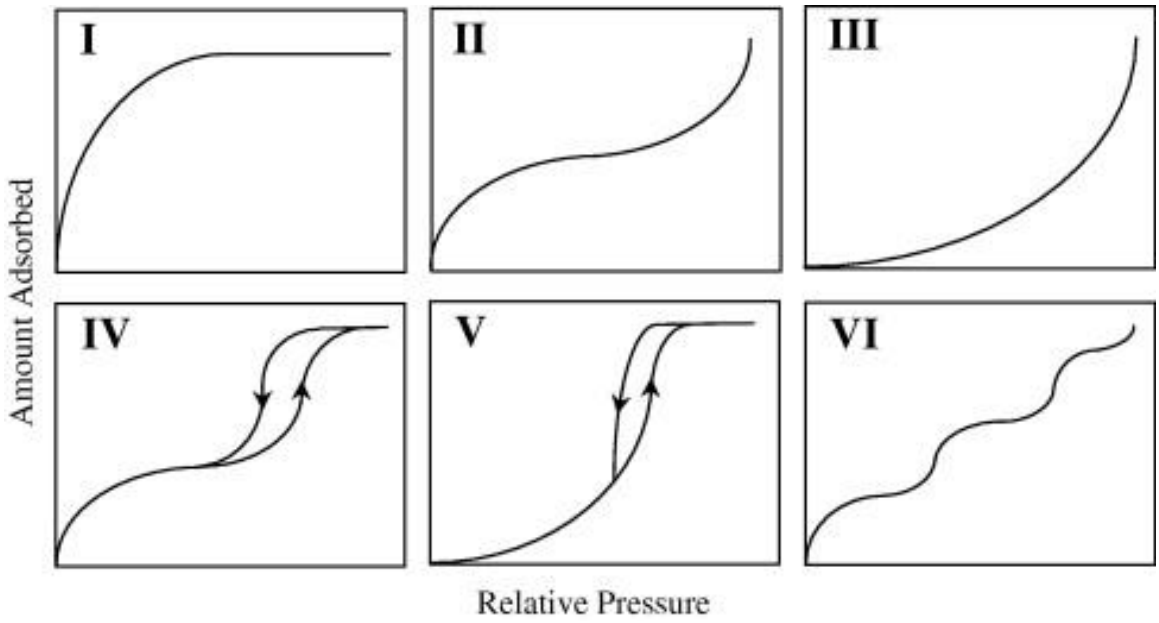


Figure 2-4. Adsorption isotherm types.

The shape of the isotherm can provide insight into the physical properties of the activated carbon particle. The following are brief insights into the various isotherm types (Marsh et al., 2006):

- Type 1: Reaches a maximum value without inflection; indicative of microporosity only with monolayer adsorption.
- Type 2: Shows an inflection point, leading to multilayer adsorption.
- Type 3: Convex shape, which is characteristic of low adsorption potential.

- Type 4: Resembles the Type 2 isotherm, but additionally, adsorption takes place in mesoporosity. Hysteresis is seen.
- Type 5: Low energy surface that contains mesoporosity. Hysteresis is seen.
- Type 6: Surface with extremely homogeneous structure. Not seen in activated carbon.

Hysteresis, which is displayed graphically in the Type 4 and 5 isotherm, is defined when the quantity adsorbed is different when material is being added than it is when being removed. Thus, there is a different relationship between amount adsorbed and relative pressure during adsorption and desorption. This phenomenon is witnessed because the mechanism of capillary condensation in the mesopores differs from that in which mesopores are emptied. The difference in nomenclature between the various pores is classified by the IUPAC-accepted criteria. The three classes of pores and their corresponding pore diameters are show in Table 2-2.

Table 2-2. IUPAC-accepted pore classification.

Pore Type	Pore Diameter (nm)
Micropores	$d_p < 2$
Mesopores	$2 < d_p < 50$
Macropores	$d_p > 50$

Most often, these isotherms are produced from the adsorption of a gas (nitrogen or argon) onto the solid phase (GAC) at the boiling point of liquid nitrogen, 77 K. Many researchers studying activated carbons for environmental engineering applications have utilized the BET methods described in Gregg & Sing (1982). This method has been used to calculate and compare the surface areas of highly microporous samples. The

adsorption of N_2 by GAC is mostly due to micropore filling, and thus, the method is best suited to determine relative changes between activated carbon samples rather than absolute measures of specific surface area (Stoehr et al., 1991).

2.3.3. Chemical Properties of Activated Carbon

The determination of chemical characteristics of the surface functional groups on an activated carbon particle can be used to correlate performance. Catalytic activity has been shown to be largely determined by the types and quantities of non-carbon elements (oxygen, nitrogen, hydrogen, phosphorus, sulfur, etc.) present in the GAC structure (Sontheimer et al., 1988). The specific composition and activity of these surface oxides on activated carbon are a function of the raw material used, activation temperature, duration of oxidizing gas exposure, and the composition of these activation gases.

Activated carbons develop either an acidic character due to the formation of carboxylic, lactonic, and phenolic hydroxyl groups (Li et al., 2002) or a basic character from the formation of pyrone and quinone groups. Chou (1986) proposed that catalytic activity of activated carbon could be enhanced by removal of acidic surface groups. Dastgheib (2004) found that activation with ammonia decreased acidity and increased basicity of activated carbon. Acidity and basicity of an activated carbon are typically determined using variations of the Boehm titration methodology (Sontheimer et al., 1988). Although the Boehm titration is a quantifiable measurement of raw acidity and basicity, it does not allow determination of the identity of the surface functional groups responsible for reactions. Various infrared (IR) transmission and internal reflection techniques have been used to identify the surface functional groups on the activated carbons (Ishizaki & Marti). Fourier-transform infrared (FTIR) spectroscopy in the mid-infrared range of 4000 to 700 cm^{-1} is commonly used to collect IR data.

2.3.4. Catalytic Reactions of Activated Carbon with Monochloramine

In 1973, Bauer and Snoeyink performed controlled batch experiments, while monitoring HOCl, NH_2Cl, $NHCl_2$, NCl_3, total N(-III), and pH to propose a reaction between GAC and monochloramine. Their conclusion took the form of a reaction mechanism that depicted the likely interaction between monochloramine and fresh activated carbon.

$$NH_2Cl + H_2O + C^* \rightarrow NH_3 + H^+ + Cl^- + CO^* \quad (2\text{-}4)$$

In equation 2-4, C^* represents an active site on the GAC while CO^* represents an acidic surface oxide formed on the GAC surface. The authors performed batch studies using fresh and pretreated activated carbon, which allowed them to find that after equation 2-4 proceeded to a specific degree, the following reaction occurred:

$$2NH_2Cl + CO^* \rightarrow N_2 + H_2O + 2H^+ + 2Cl^- + C^* \quad (2\text{-}5)$$

In equation 2-5, the monochloramine nitrogen is oxidized completely to nitrogen gas while chlorine is reduced to chloride ion. The authors concluded that while the GAC is being acclimated, the monochloramine is converted to ammonia, while nitrogen gas is formed only when a certain degree of acidic surface oxides (CO^*) have been formed.

To extend this work, Kim (1977) applied this reaction mechanism to GAC-monochloramine FBR studies. The guiding hypothesis of this research was that a steady state monochloramine concentration would result from the reactions presented in Equations 2-4 and 2-5 proceeding in parallel. In short, one reaction would produce surface oxides while the other would consume them. Kim was able to demonstrate that steady state conditions developed after a period of higher removal.

Several researchers have attempted to experimentally and theoretically determine the pH dependencies of these reactions. It was noted that the pH dependent speciation of various chloramines could translate into GAC-monochloramine reactions that are

correspondingly pH dependent (Jafvert and Valentine, 1992). Furthermore, there was a possibility that the surface functional groups responsible for participation in the monochloramine reduction could have acid dissociation constants (pKa's) within the pH 7-9 chloramination range.

Work at the University of Texas confirmed steady state monochloramine removal that was increasingly evident with modified catalytic activated carbons (Fairey et al., 2006). These results supported the reaction sequence previously proposed. Furthermore, the authors evaluated the pH dependencies of these reactions, noting that pH had a significant effect on GAC-monochloramine reactions.

2.3.5. Catalysis vs. Adsorption with Activated Carbon

In typical adsorption processes, atoms, ions, or molecules are attracted to a surface, and then adhere there. This phenomenon is a function of various surface forces; most adsorption is characteristic of weak van der Waals forces, while certain processes involve chemical or electrostatic attraction. The surface of the adsorbent contains a finite area in which molecules are retained. Because there are limited adsorption sites, the activated carbon material is no longer able to adsorb material once the capacity has been reached. Any further contaminant introduced into the system will break through into the effluent.

In a surface catalyzed process, the destruction of the substrate (monochloramine) frees up sites while new substrate is destroyed, resulting in steady state effluent substrate concentrations from fixed bed reactors (FBRs) that are lower than the influent concentration even after the expected sorption capacity of the surface has been exceeded. Activated carbon FBR performance is typically expressed as a breakthrough curve. This curve plots the dimensionless effluent concentration (C_{eff}/C_{in}) over the time that the

experiment or pilot study is performed. Figure 2-5 depicts two breakthrough curves, which highlight the differences one would expect from a traditional adsorption versus a catalytic process. Breakthrough is easily distinguishable in the adsorption process, where the C_{eff}/C_{in} value approaches 1; i.e. there is no removal as the effluent concentration reaches the same value as the influent. Conversely, the catalytic process reaches a steady state value that is some degree lower than the influent concentration. In the case of GAC-monochloramine reactions, one can assume this steady state is reached when the rate at which CO* is produced (Equation 2-4) is equal to that at which CO* is consumed (Equation 2-5).

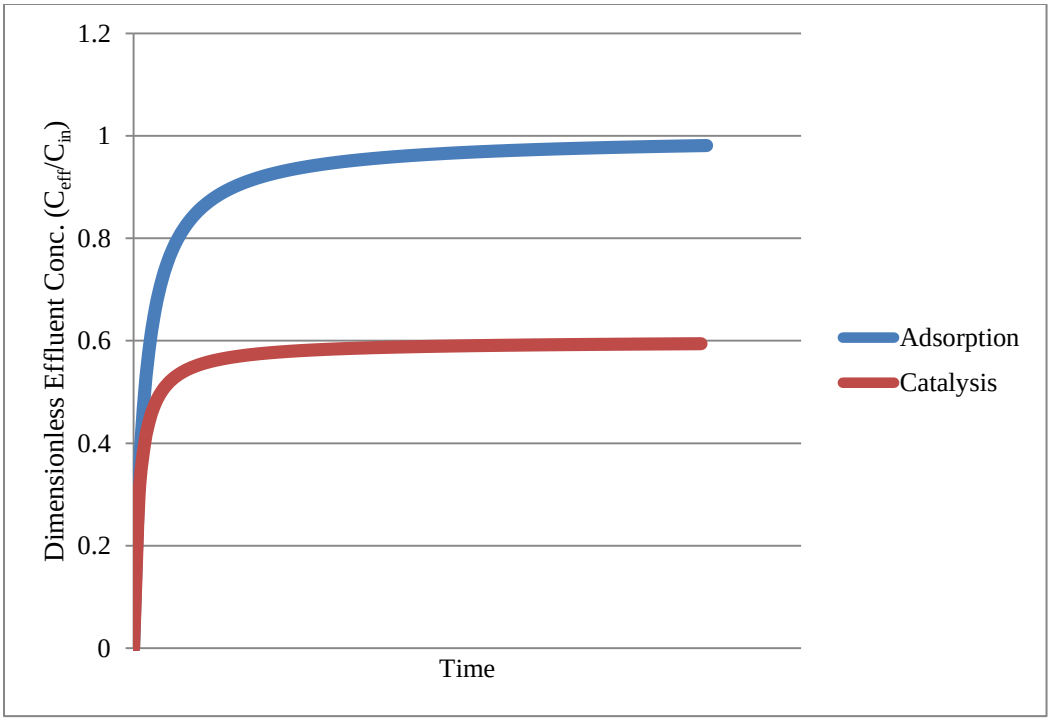


Figure 2-5. Breakthrough curve depicting adsorption vs. catalysis.

2.3.6. Fixed Bed Reactor Design and Terminology

One of the key parameters that influence the operation of an activated carbon column, or FBR, is the empty bed contact time (EBCT). This parameter is a measure of how much contact occurs between the adsorbent (GAC) and the water as it flows through the bed. It is calculated via the following equation:

$$EBCT = V/Q \tag{2-6}$$

In equation 2-6, V represents the volume of the column or fixed bed reactor, without any media; Q represents the volumetric flow rate, which should remain nearly constant during operation. As the EBCT increases, the time available for GAC particles to adsorb solutes from the water also increases. Thus, higher removal efficiency is expected as the contact time increases.

In 1980, Kim and Snoeyink hypothesized that the GAC-monochloramine reactions took place in three steps: adsorption, surface reaction, and desorption. In any GAC FBR, there are three fundamental types of mass transport that are involved. Before the solute can reach the surface of the particle, diffusion through the liquid film boundary layer must occur. This process is denoted film diffusion. After, the compound must reach a reaction site within the GAC pores by diffusing into the internal surfaces of the particle. This process can occur by diffusion into liquid filled pores (pore diffusion) or along the walls of the pores (surface diffusion); in reality, both pore and surface diffusion can occur simultaneously. Figure 2-6 depicts each of the aforementioned mass transport processes.

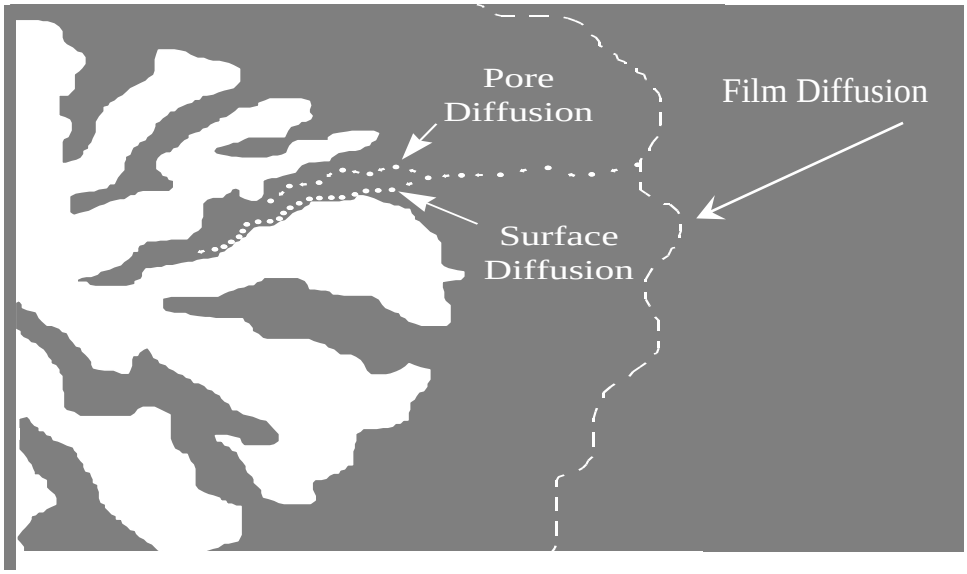


Figure 2-6. Mass transport processes relevant to GAC FBRs.

2.4. MONOCHLORAMINE CATALYSIS WITH GAC MODEL

In 1977, Kim introduced a numerical model that predicted monochloramine removal for GAC particle sizes used in industry based on calibration with laboratory scale results. In 2006, Fairey et al. applied this model to predict full scale performance with modified catalytic activated carbons. The model is referred to by Fairey (2006) as the MCAT model. MCAT results for steady state operation were verified by lab studies to be a conservative, yet very good approximation of reality. This model incorporated pore diffusion as the rate limiting mechanism. Liquid film diffusion and surface diffusion were not included in the model and were assumed to be negligible. Furthermore, the non-catalyzed disappearance of monochloramine was neglected; this was justified by the relatively short residence time of the column. A mass balance on monochloramine in the pore phase at steady state gives:

$$\frac{d^2C}{d\xi^2} = \frac{4}{d_p}\frac{{L_p}^2}{D_C} R_C(C) = 0 \text{, at } 0< \xi <1 \qquad (2\text{-}7)$$

$$\text{at } \xi = 0, \ \frac{dC}{d\xi} = 0$$

In Equation 2-7, C is the concentration of monochloramine, D_C is the bulk diffusivity of the chlorine species (a function of water temperature), ξ is the reduced position variable measured from the center of the pore, and R_C is the rate of monochloramine reaction on the surface. L_p represents the effective diffusional path length and is defined as one-sixth of the arithmetic mean of the particle size range. A mass balance on the bulk fluid at steady state in the FBR gives:

$$\beta\frac{d^2C_B}{d\alpha^2} + \delta\frac{dC_B}{d\alpha}\tau\frac{dC}{d\xi}\Big|_{\xi=1} = 0 \text{, at } 0< \alpha <1 \qquad (2\text{-}8)$$

$$\text{where } \beta = \frac{D_A}{D_C}\frac{{L_p}^2}{{L_b}^2}, \ \delta = \frac{{L_p}^2}{D_C}\frac{\nu}{L_b}, \text{ and } \tau = \frac{m}{\varepsilon}V_p$$

$$\text{at } \alpha=1, \ C_0 = C_B + \frac{D_A}{L_b\nu}\frac{dC_B}{d\alpha} \text{ and at } \alpha=0, \ \frac{dC_B}{d\alpha} = 0$$

In Equation 2-8, D_A is an axial dispersion coefficient, L_b is the length of the packed-bed reactor, ν is the average solution interstitial velocity, m is the mass of carbon per unit volume of reactor, ε is the reactor porosity, V_p is the pore volume of the carbon per unit mass, C_0 is the influent monochloramine concentration, C_B is the bulk monochloramine concentration, and α is the reduced position variable in the packed-bed reactor (inlet at $\alpha = 0$).

The reaction term, R_C, which appears in Equation 2-7 was empirically derived. All attempts to obtain a surface reaction rate assuming a mechanism were unsuccessful. The empirical reaction expression is:

$$R_C = {f_2}^2\left(\frac{C}{C+f_1}\right)^2\left(1+\frac{f_3Q^3}{1+f_4Q^3}+\frac{f_5}{f_6}-\frac{f_5Q^3}{1+f_6Q^3}\right) \qquad (2\text{-}9)$$

However, at steady state, the mass of monochloramine reacted per unit weight of carbon (Q) becomes large, which simplifies the expression to:

$$R_C = f_7\left(\frac{C}{C + f_1}\right)^2 \tag{2-10}$$

In Equation 2-10, f_1 and f_7 are rate constants that are determined by fitting the model to experimental data; C is the monochloramine concentration (mg/L as Cl_2) and $f_7 = f_2{}^2(1+\frac{f_3}{f_4})$.

The partial differential equations contained in the MCAT model are reduced to a set of ordinary differential equations in time using orthogonal collocation. The solver used to obtain a solution for the stiff equations is based on Gear's Method. Fairey et al. (2006) used this model to conclude that steady state operation with modified activated carbons could be feasible for certain applications. This result is more optimistic than the results of Komorita and Snoeyink (1985), who concluded steady state operation required unrealistically large EBCTs with traditional GACs.

Chapter 3: Materials and Methods

3.1. OVERVIEW

The following chapter outlines the materials and methods that were utilized to complete the three phases of the project. Overall, these methods were carried out to quantify the steady state reduction of monochloramine in FBRs, determine the optimal activated carbon sample for removal, improve understanding of physical and chemical properties that influence removal, and model full scale performance in point of use applications. It is noted that many of the methods and experiments employed in this research were adapted from the work of Fairey et al. (2006).

To assess the capabilities for steady state reduction of monochloramine by the selected activated carbons, a fixed bed reactor experimental setup was created to monitor the influent and effluent concentration over the duration of the study. Three commercially available activated carbons currently incorporated in point of use filters were tested using influent City of Austin tap water. To characterize the physical properties of the activated carbon, nitrogen gas isotherms at 77K were analyzed for each of the virgin samples. Specific surface area, pore volume, and pore size distribution were determined from the results of the nitrogen adsorption. Chemical properties of the samples were tested by performing Boehm Titrations to determine acidity and basicity. To qualitatively identify the surface functional groups on the GAC particle, Fourier Transform Infrared (FTIR) Spectroscopy was conducted on each of the virgin activated carbon samples. After calibrations, the MCAT model was used to simulate performance in full scale point of use filters for various conditions of interest.

3.2. FIXED BED REACTOR STUDIES

3.2.1. Granular Activated Carbon Samples

Three GAC samples were considered during this project: Jacobi AquaSorb CX-MCA (Jacobi CAT), Norit Catalytic Carbon (Norit CAT), and Norit Coconut Shell Carbon (Norit CNS). Each of these three activated carbons was selected due to claims regarding their potential for removal of monochloramine from chloraminated drinking water. Furthermore, they are currently being used in point of use filter applications, lending real-world implications to this research. Finally, the goal in selection of activated carbons was to select carbons derived from different base materials and activated under different conditions. The manufacturer, raw materials, and activation gases used for each GAC sample are shown in Table 3-1. The manufacturers of Jacobi CAT claim that the propriety catalytic activation of the coconut shell charcoal makes it highly effective for the removal of chloramines. Furthermore, Jacobi claims that the large micropore volume contained in the structure of the carbon particle makes it particularly well suited for removal of small compounds, such as monochloramine. Both Jacobi CAT and Norit CNS were made from coconut shell as a base material, while Norit CAT was made from bituminous coal. With regards to activation gases, Jacobi CAT and Norit CAT were treated with steam and a propriety catalytic gas treatment while Norit CNS was treated with only steam.

Table 3-1. Selected propertied of GACs analyzed.

GAC	Manufacturer	Raw Material	Activation Gas
Jacobi CAT	Jacobi Carbons, Inc. Columbus, OH	Coconut Shell	Steam, catalytic proprietary treatment
Norit CAT	Norit Americas, Inc. Marshall, Texas	Bituminous Coal	Steam, catalytic proprietary treatment
Norit CNS	Norit Americas, Inc. Marshall, Texas	Coconut Shell	Steam

Each of these GACs was obtained from the manufacturer in the US 12 X 40 mesh fraction. However, this size was too large to meet hydrodynamic considerations with regards to the laboratory scale column setup. Therefore, each of the carbons was mechanically ground and sieved to the US 40 X 50 mesh fraction. The carbon meeting the size requirement was washed in Millipore water until no more fines existed. Then, each activated carbon was equilibrated with Millipore water for 24 hrs. The carbon was washed again, decanted, dried in a 100°C oven for 24 hours, and stored in a desiccator until use. Packed bed density was calculated by dividing the dry mass of the carbon placed in each column by the volume of the column.

3.2.2. Influent Water Source

The purpose of this study was to evaluate the effectiveness of GACs in point of use filters. Since these filters are typically used with tap water, it was decided to use tap water as the influent water source. Treated water from the City of Austin, TX was selected. This water was constantly obtained from the tap, to represent the minor fluctuations in water characteristics that result from ever-changing demand. On average, the influent monochloramine concentration was measured around 1.5 mg/L as Cl_2. To minimize plugging of the FBRs, the tap water was filtered through a 0.2-um Polycap 75 AS filter (Whatman, Piscataway, NJ) to remove any particulate matter that had been

picked up in the distribution system. Table 3-2 provides the City of Austin Water Quality Summary from January 1, 2012 to March 31, 2012, which corresponds to the time that experiments were conducted. DWTP and UWTP correspond to the Davis and Ulrich Water Treatment Plants; these are the providers of City of Austin water. From the table, the relatively high pH at the tap of 9.6 can be seen. To bring the pH to a consistent value necessary for experiments, sulfuric acid or sodium hydroxide was added.

Table 3-2. City of Austin Water Quality Summary 1st Quarter Averages (January 1, 2012 to March 31, 2012).

CONSTITUENT (mg/L)	DWTP Raw	UWTP Raw	DWTP Tap	UWTP Tap	SDWA Tap MCL/[SMCL]
Total Ammonia (as N)	---	---	0.52	0.57	
Free Ammonia (as N)	---	---	0.08	0.13	
Calcium	50	50	12	16	
Chlorine Residual	---	---	2.58	2.52	
Fluoride	0.24	0.24	0.57	0.73	4/[2]
Magnesium	22	22	20	18	
Sulfate	37.3	37.0	47.9	42.6	[250]
Total Phosphate	0.03	0.03	0.96	0.62	
Total Hardness (as $CaCO_3$)	214	216	111	112	
pH (units)	8.2	8.3	9.6	9.6	[>7.0]
Conductivity (umhos/cm)	539	534	374	375	
Total Alkalinity (as $CaCO_3$)	174	174	68	69	
Phenol Alkalinity (as $CaCO_3$)	0	0	16	17	
Total Solids	316	311	210	211	[500]
Threshold Odor (TON)	4	4	0	0	[3]
Total Organic Carbon	3.57	3.71	2.68	2.57	
Turbidity (NTU)	2.73	2.79	0.08	0.04	0.3
Silica	7.6	7.7	6.8	6.8	
UV254 (cm^{-1})	0.070	0.080	0.060	0.060	
Total Coliform (Col/100ml)	121	210	<1	<1	
E.Coli (Col/100ml)	30	24	<1	<1	

Parameters listed below were analyzed by the Texas Department of State Health Services for compliance with the Safe Drinking Water Act.

Also noteworthy from Table 3-2 is the Total Organic Carbon values of 2.68 and 2.57 for tap water from DWTP and UWTP, respectively. Fairey et al. (2006) showed the significant impacts of NOM on the GAC catalyzed removal of monochloramine.

3.2.3. Experimental Setup

To perform the FBR studies, an experimental setup was developed that allowed isolation of several variables, while holding other parameters constant. Figure 3-1 depicts a diagram of the experimental setup used in this research. Tap water was supplied to the constant head tap water feed tank. Also connecting to the feed tank was an overflow line; this allowed the water in the tank to stay at a constant level throughout the entirety of the experiment. In terms of performance, the constant water level setup avoided variations in flow rate due to changes in upstream head. From the tank, water was pumped through the 0.2-μm filter to the mixing chamber. The mixing chamber is where addition of sulfuric acid or sodium hydroxide was staged.

Upon vigorous mixing, a peristaltic pump was used to deliver the influent water stream to each of the three column lines at the same flow rate. The three parallel column lines were operated in an up flow configuration, to facilitate the removal of nitrogen gas generated from catalytic GAC-monochloramine reactions. Each of the three column lines had three columns operated in series. Sampling ports were located before the first column, as well as after each of the columns in series. This allowed for measurement of chloramine concentrations of the influent and effluent streams for each column in series.

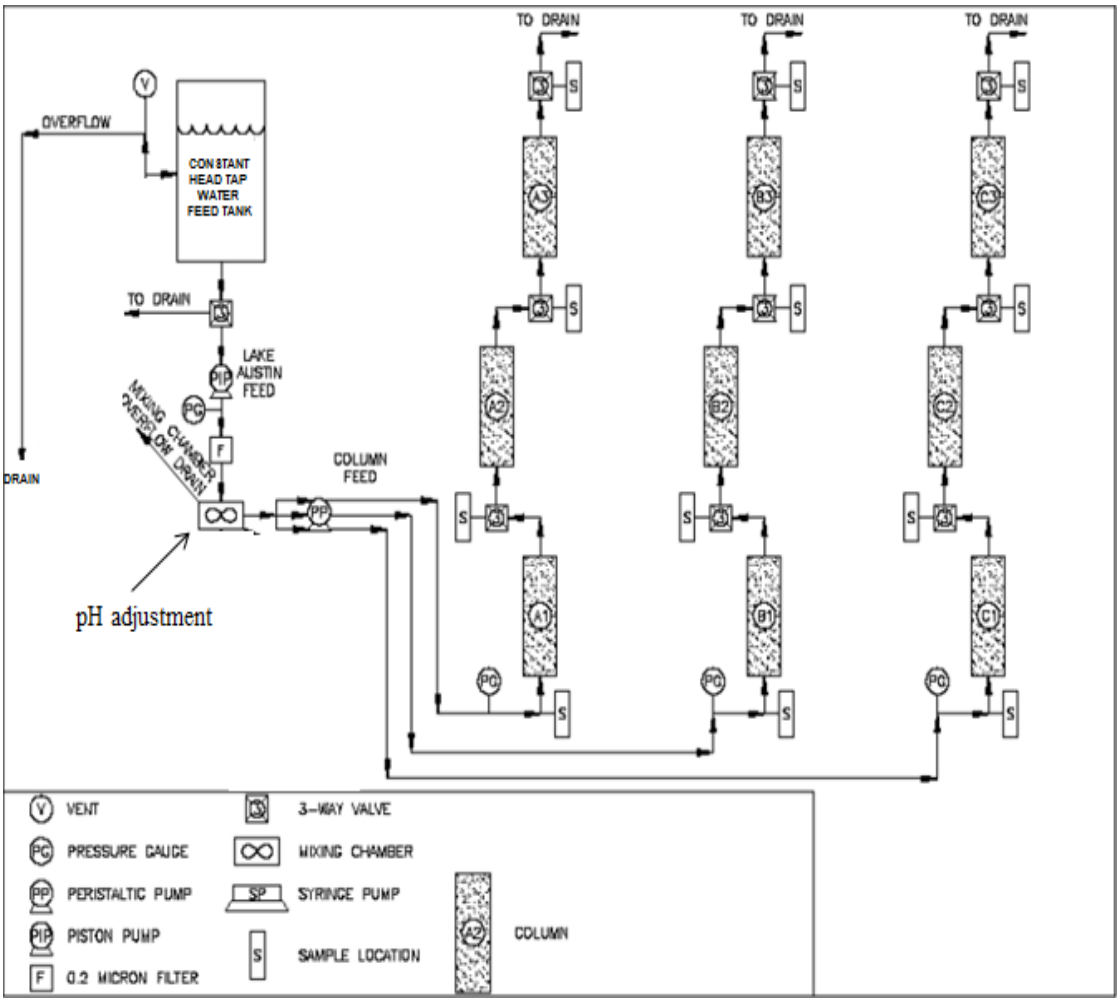


Figure 3-1. Detailed schematic of setup for fixed bed reactor studies.

Overall, this experimental setup allowed testing of the three different GAC types (1 per parallel column line) at three different EBCTs each (effluent from each of the columns in series). In the given experiment, the activated carbon's performance could be evaluated as a function of GAC type and EBCT. A photograph of the entire experimental setup is located in Figure 3-2 while a closer view of the column trains is shown in Figure 3-3.

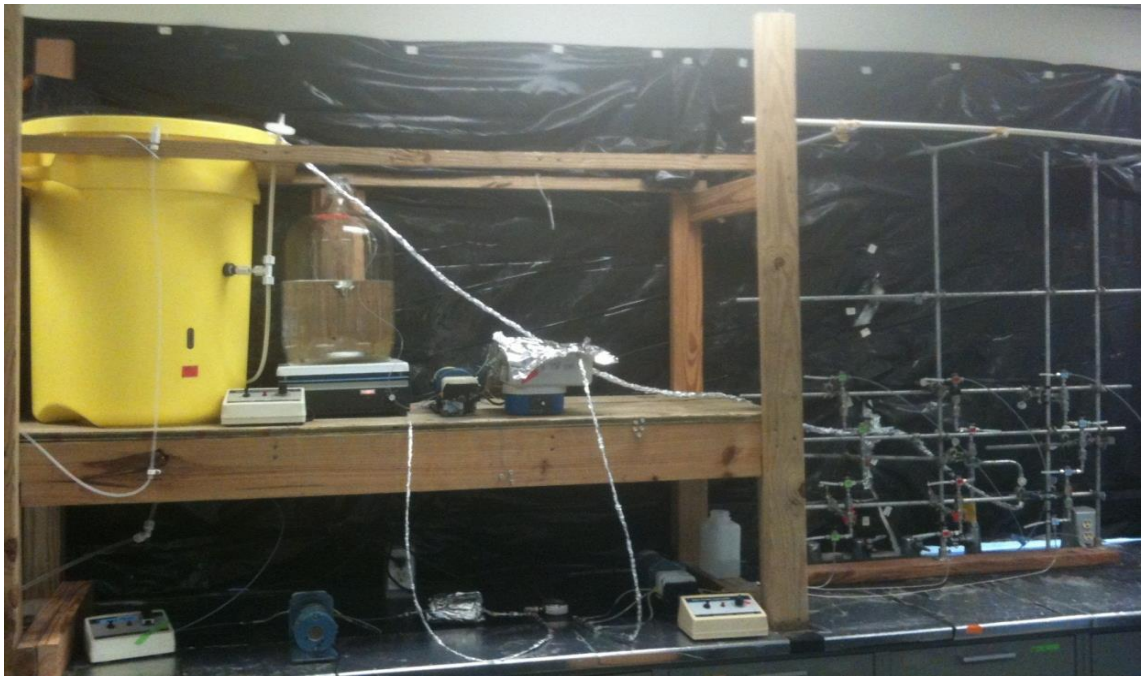


Figure 3-2. Photograph of the experimental setup used for the FBR studies.

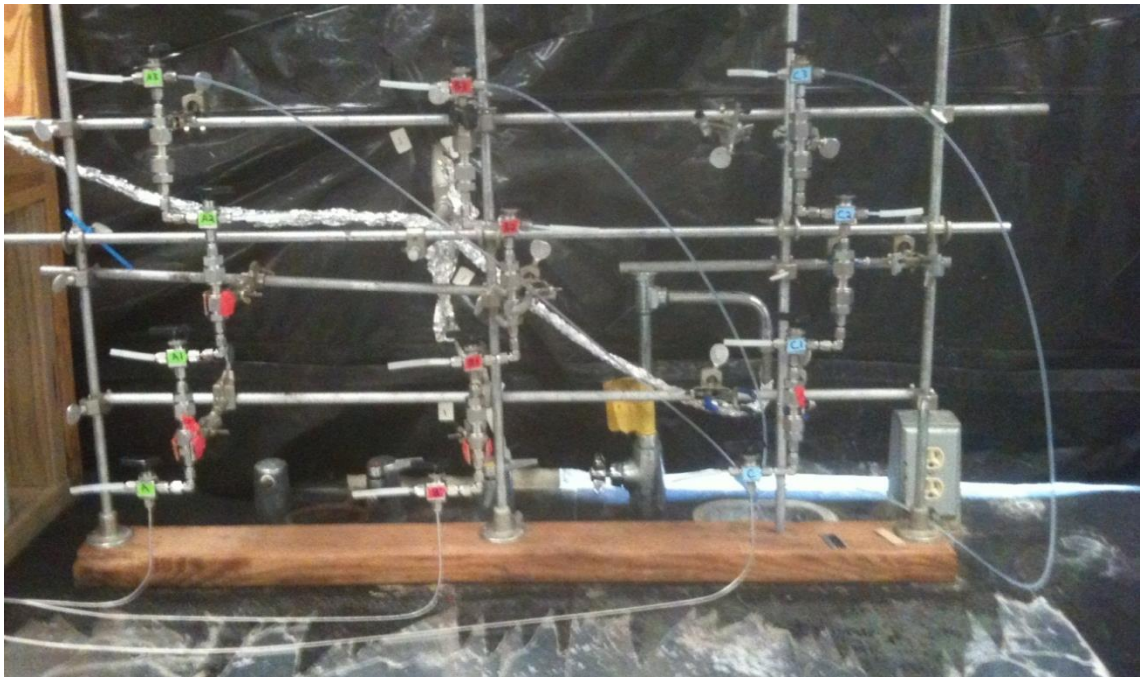


Figure 3-3. Closer view of column trains used in the FBR studies.

The entire setup was erected from 316 stainless steel to prevent monochloramine reactions with the columns or flow transfer lines. Certain tubing needed to be flexible to facilitate proper construction. In these instances, HDPE tubing with Teflon coating was used, which is considered to be inert with respect to monochloramine. Figure 3-2 shows that the windows behind the experimental setup were blocked and all clear lines and the mixing chamber were wrapped in aluminum foil. These precautions were enacted to avoid potential light-degradation of monochloramine prior to entering the GAC columns. Initially, the experimental setup was operated at pH 8; after reaching a steady state effluent monochloramine concentration, the pH was shifted to 9, and a new steady state effluent was approached. To compare results with EBCTs commonly used in point of use home filters, EBCTs of 0.25, 0.5, and 0.75 min were tested. Flow rate was held constant at 8.0 mL/min, consistent with the work of Fairey et al. (2006). Jacobi CAT, Norit CAT, and Norit CNS were placed in column trains A, B, and C, respectively. All of the experimental conditions relevant to the FBR studies are shown in Table 3-3.

Table 3-3. Summary of experimental conditions for FBR studies.

Column Line A	Jacobi CAT	
Column Line B	Norit CAT	
Column Line C	Norit CNS	
Target pH	8.0 (0.2)	After SS, 9.0 (0.2)
Flow Rate per Column	8.0 (0.2)	mL/min
Bed Diameter	1	cm
Bed Length	2.55, 5.1, 7.65	cm
EBCT	0.25, 0.50, 0.75	min
Carbon Grain Size	US 40 X 50 sieve	
Target Influent Conc.	1.5	mg/L as Cl_2

The calculated surface loading rate to each of the reactors was 6.11 m/hr. This is identical to the rate used by Fairey et al. (2006) and is supported by Kim and Snoeyink (1980b). There, the authors showed that their assumption of negligible film resistance in the MCAT packed bed model was valid over the range of 2.4 to 28.8 m/hr for 12 X 40, 40 X 50, and 60 X 80 US mesh size particles. Also of importance is the ratio of bed diameter to geometric mean GAC particle size. Rose (1951) showed that this ratio must be at least 30 to inhibit the influence of hydraulic wall effects.

In summary the FBR studies corresponding to this research encompassed three activated carbon types at three different EBCTs each at a pH of 8.0 and 9.0. At the end of the study, 18 unique combinations were tested in this phase of research.

3.3. AQUEOUS ANALYSES

3.3.1. Monochloramine Measurement

Monochloramine was measured using Hach Method 10171. 10 mL of sample was mixed with 1 Hach Monochlor F pillow packet for 20 seconds. Upon completion, exactly 5 minutes of development time was needed before measurement. Absorbance was then measured on the UV-visible spectrophotometer (Agilent 8453) at 655 nm using a 1.0 cm cell length cuvette. Calibrated standards were created between 0.0152 and 1.52 mg/L as Cl_2. The calibration curve, shown in Figure 3-4, was used to convert absorbance measurements at 655 nm to monochloramine concentration in mg/L as Cl_2.

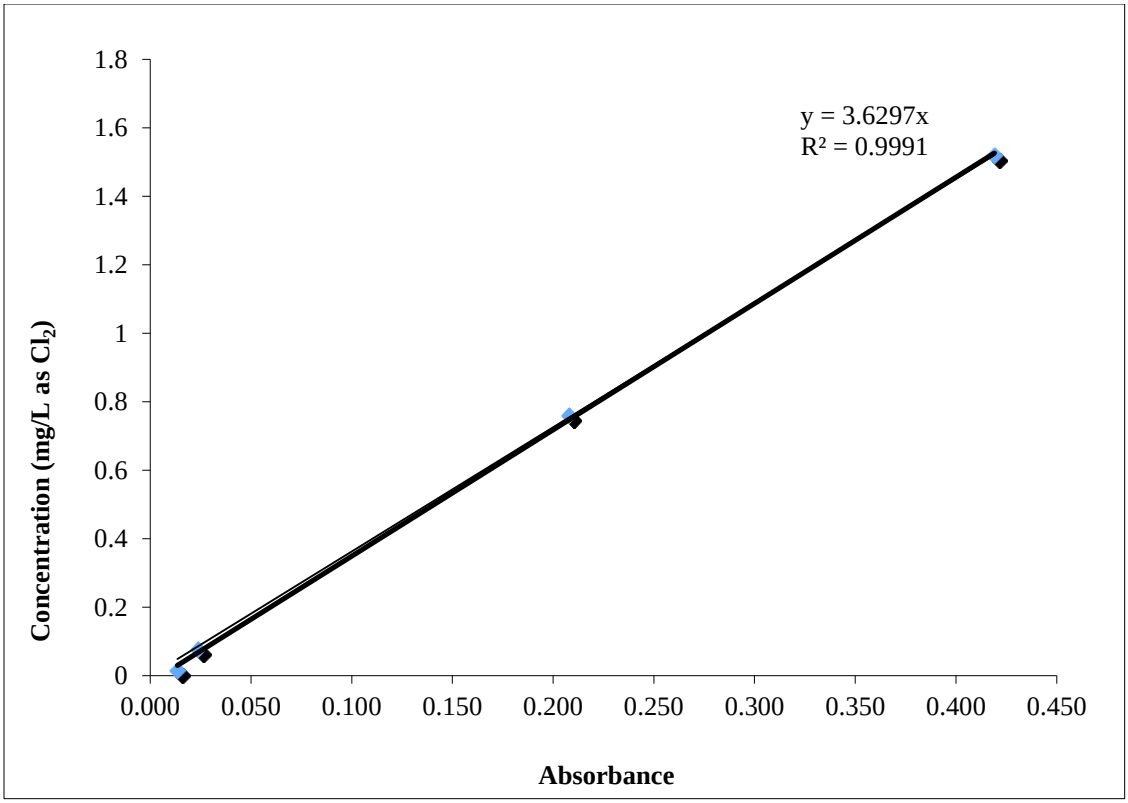


Figure 3-4. Monochloramine calibration curve.

3.3.2. pH Measurement

The pH of each water sample involved in the FBR studies, as well as the supernatant during Boehm titrations was measured on an Orion Star A211 pH electrode (ThermoScientific, West Palm Beach FL). Prior to each analysis, the pH instrument was calibrated with certified pH standards of 4, 7, and 10.

3.4. GAC ANALYSES

3.4.1. Physical Characterization using Nitrogen Gas Adsorption Isotherms

Physical properties of the activated carbon samples were determined by analysis of nitrogen gas adsorption isotherms at 77 K. A Quantachrome Autosorb surface area

analyzer with independent degassing control was utilized for this purpose. To perform the analysis, a known mass of GAC sample was placed in a sample tube; it was placed in an isothermal jacket and degasified under vacuum at 250 °C for at least 48 hours to remove any pore water. The sample was then re-weighed to obtain an accurate measurement of the dry mass, and transferred again to the sampling port on the Autosorb instrument. There, the sample was degassed again to remove any water that had accumulated during the transfer. The instrument software performed the adsorption/desorption analysis with the conditions specified in Table 3-4.

Table 3-4. Analysis conditions specific in Autosorb software for N_2 adsorption isotherm.

Parameter	Comment
Equilibration Interval	45 seconds
Low Pressure Dose	3 cm^3/g
Minimum Equilibration Delay	000
Maximum Equilibration Delay	999

After the adsorption/desorption isotherm was generated, the surface area, pore volume, and pore size distribution were calculated from analysis of the isotherm. Previously documented procedures used in the work of Fairey et al. (2006) adapted from Gregg & Sing, 1982, were used. To summarize the analysis techniques used, the specific surface area of each of the activated carbon samples was determined by applying the BET equation in the relative pressure range of 0.01 to 0.10. The total pore volume was calculated from conversion of the adsorbed volume of nitrogen gas at the relative pressure of 0.98. Micropore volume was obtained using the Dubinin-Radushkevich equation in the relative pressure range of 10^{-5} to 10^{-1}; Mesopore volume was approximated as the difference between the total pore volume and the micropore volume for each respective GAC sample.

3.4.2. Total Acidity and Basicity Using Boehm Titration Method

Total acidity and basicity of each activated carbon sample was quantified by NaOH and HCl uptake, respectively (Boehm 2002). Triplicate samples of 0.100 g of each carbon in the US 40 X 50 mesh size were placed in 25 mL glass vials with either 20 mL of 0.05 N NaOH or 20 mL of 0.05 N HCl. Each GAC type was equilibrated for 7 days with both acid and base. During the equilibration period, the samples were tumbled end over end to ensure equilibrium was attained. Furthermore, blank vials were created with either NaOH or HCl, without GAC to provide an accurate representation of any acid/base change during the 7 days not attributable to interactions with the activated carbon. Prior to titrating, the HCl solution was standardized with Na_2CO_3 and the NaOH was then standardized with the HCl solution. 10 mL of supernatant was obtained from the vials and the concentration of NaOH or HCl remaining was calculated via titration. The back-titration was conducted with a 1000-µL pipette for most additions; however, smaller volumes near the equivalence point were injected using a 20-200 µL pipette (Rainin, Oakland CA). The total acidity was calculated as the difference between the blank NaOH sample and the average of the samples equilibrated with NaOH. Total basicity was calculated in the same manner using the HCl samples. The uptake was converted to equivalents of NaOH or HCl per gram of GAC. A theoretical titration curve using HCl to titrate NaOH concentration is presented in Figure 3-5 to provide a graphical representation of the Boehm Titration methodology.

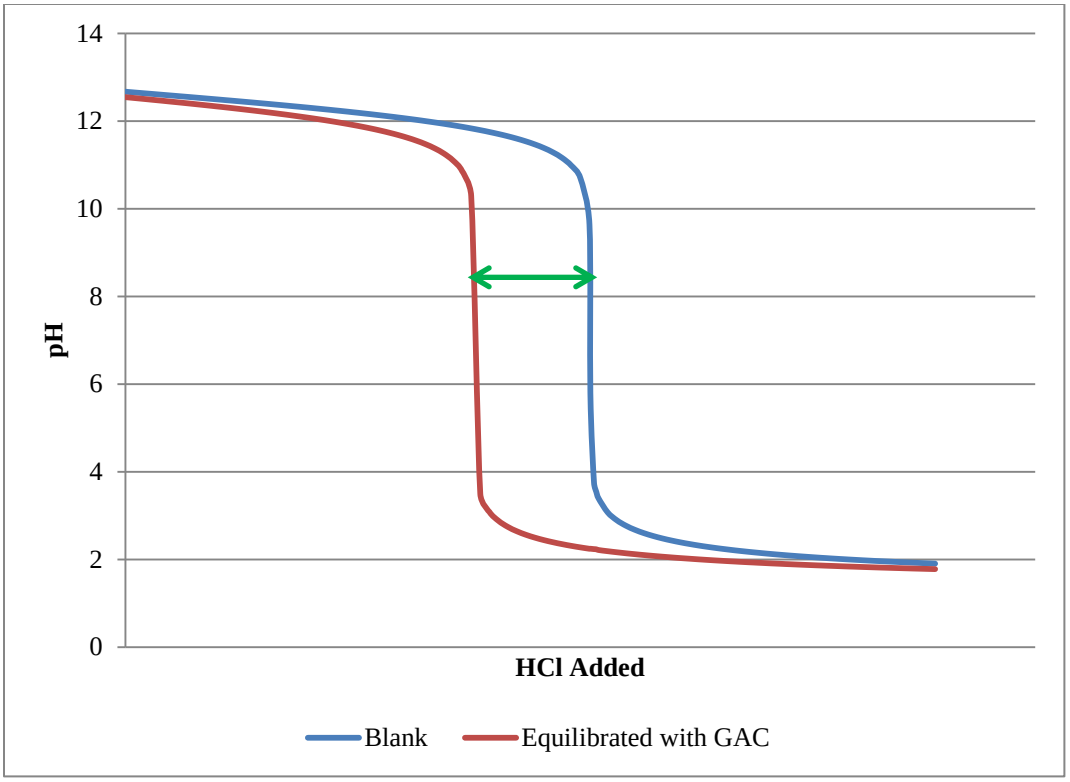


Figure 3-5. Theoretical NaOH uptake curve to represent Boehm Titration method.

From the curve, the Boehm titration method is apparent. The difference in HCl added to reach the equivalence point (pH equal to 7 for strong acid/base system) from the blank and the samples equilibrated with GAC represents the amount of NaOH consumed by acidic functional groups on the activated carbon surface. This is represented by the green double arrow in Figure 3-5. Since the titration procedure was performed in an open atmosphere, it is possible that the carbonate system could infiltrate the solutions, most probably the NaOH solution. However, since this phenomenon would occur in the blank and the sample, the Boehm Titration results are unaffected.

3.4.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to qualitatively assess the identity of the surface function groups that are present on each of the GAC samples. Transmission spectra were measured on a Bruker IFS 66v/S single channel FTIR spectrophotometer using procedures similar to Fairey et al. (2006) adapted from Vinke et al. (1993). GAC samples were pulverized with a mortar and pestle for 10 minutes each. These samples were mixed in a 1 % mass ratio with pulverized potassium bromide (KBr) and then transferred to glass vials for storage. Prior to the analysis, samples were placed in a desiccator for at least 24 hours. Samples were contained in a Praying Mantis (Harrick, Ossining NY) sample holder with low volume cup. The sample chamber was evacuated to 2 mbar during measurement. Spectra were created with a liquid nitrogen cooled narrow-band mercury cadmium telluride (MCT) detector by co-addition of 500 scans at a resolution of 4 cm^{-1} in the mid-infrared range of 4000 to 700 cm^{-1}. A pure KBr sample was run prior to analyzing samples, and served as a blank that was subtracted from GAC sample spectra to indicate the true response of the samples. The corresponding spectra were corrected using a curved baseline feature in the OPUS software used for strongly scattering samples.

3.5. MODELING

Modeling full scale performance of the GAC catalyzed destruction of monochloramine was performed using the packed bed monochloramine catalysis (MCAT) model developed by Kim in 1977. The use of the model to make steady state predictions of performance in systems with GAC particle sizes used in practice was highlighted in the work of Fairey et al. (2006). Central to the use of the model for steady state predictions is the surface reaction expression that was empirically derived by Kim

from fitting experimental data to the MCAT model. The parameters for this model are highlighted in the following expression:

$$R_C = f_2{}^2\left(\frac{C}{C+f_1}\right)^2\left(1+\frac{f_3Q^3}{1+f_4Q^3}+\frac{f_5}{f_6}-\frac{f_5Q^3}{1+f_6Q^3}\right)$$

However, steady state predictions with the MCAT model cause the mass of monochloramine reacted per unit mass of carbon (Q) to become large, simplifying the expression to:

$$R_C = f_7\left(\frac{C}{C+f_1}\right)^2$$

To calibrate the model, f_1 and f_7 had to be specified using experimental results from the FBR column studies. This was done by minimizing the sum of square residuals (SSR) between steady state experimental data for each EBCT test with the model generated fit. In research conducted by Fairey (2006), it was noted that multiple combinations of f_1 and f_7 resulted in nearly the same SSR for a given condition, such as GAC type, background water, and pH. Thus, it was shown that the surface reaction rate R_C was essentially dependent only on the ratio of $f_7/(f_1{}^2)$. Similar results were shown in this research. Therefore, the value of f_1 was fixed at 100 mg/L as Cl_2 for all conditions and the value of f_7 was determined by convergence to experimental data by minimizing the SSR.

A calibration was performed for each of the six conditions tested in the FBR studies. Thus, each of the three GACs at pH 8.0 and 9.0 were considered in modeling efforts. The steady state predictions were performed with the most commonly used GAC particle size in practice, the US 12 X 40 mesh size. Furthermore, to represent point of use applications, influent concentrations of 1.0, 2.0, and 3.0 mg/L as Cl_2 were modeled. These concentrations are within the typical range of tap waters.

3.6. SUMMARY

Each of the aforementioned procedures were enacted to complete all three phases of the research by (1) quantifying steady state monochloramine removal in fixed bed reactors for three GACs of interest for point of use applications, (2) furthering the understanding of physical and chemical properties that influence GAC-monochloramine catalysis in an attempt to identify optimum characteristics for point of use filters, and (3) translating laboratory scale testing to full scale simulations using a model to test the feasibility of point of use applications. In the FBR studies, Jacobi CAT, Norit CAT, and Norit CNS represented activated carbons encompassing a range of raw materials and activation strategies. The studies were performed using tap water in the pre-defined experimental setup. Physical characteristics were evaluated by analysis of nitrogen gas adsorption isotherms. Specific surface area, pore volume, and pore size distribution were evaluated. Chemical properties were evaluated using acid/base uptake titrations for quantitative analysis and qualitatively using FTIR spectroscopy. Finally, the previously developed MCAT model was used to scale experimental results to full scale applications.

Chapter 4: Results and Discussion

4.1. Overview

The overall objective of this research was to evaluate several commercially available GACs for their potential to remove monochloramine from tap water in point of use filters. The guiding hypothesis was that the physical and chemical properties of the activated carbons would influence the removal efficiency during steady state operation.

To meet this objective, three phases of research were conducted. The first phase involved a laboratory scale column study, or FBR study. The performance of three different GAC samples at pH 8.0 and 9.0 were quantified experimentally. This pH range is typical of many drinking water applications. In the second phase of research, the physical and chemical properties of each activated carbon were evaluated and correlated to the performance in the FBR studies. Physical properties were based on results from nitrogen gas adsorption isotherms; chemical characterizations were obtained with Boehm Titration methods and through analysis of FTIR spectra. In the third phase of research, results from the first two phases were used to calibrate a predictive model that incorporates a rate expression for monochloramine catalysis by GAC. Rate parameters for each sample at each pH condition were determined. Simulations of the steady state performance of each activated carbon at each pH were given using results of the MCAT model for various influent monochloramine concentrations. The implications to point of use applications were evaluated using the modeling results in conjunction with guidelines used by filter manufacturers.

The following chapter contains results and corresponding discussion for each of the three phases encompassed by this research.

4.2. FIXED BED REACTOR STUDIES

The experimental FBR system discussed in Chapter 3 was utilized to monitor influent and effluent monochloramine concentration as a function of time. The system was run with three activated carbon samples, Jacobi CAT, Norit CAT, and Norit CNS. The experiment was monitored for three different EBCTs, 0.25, 0.5, and 0.75 minutes. Figure 4-1 presents the monochloramine breakthrough curve from the FBR study at the 0.25 minute EBCT. Appendix A contains raw breakthrough curves from the FBR studies.

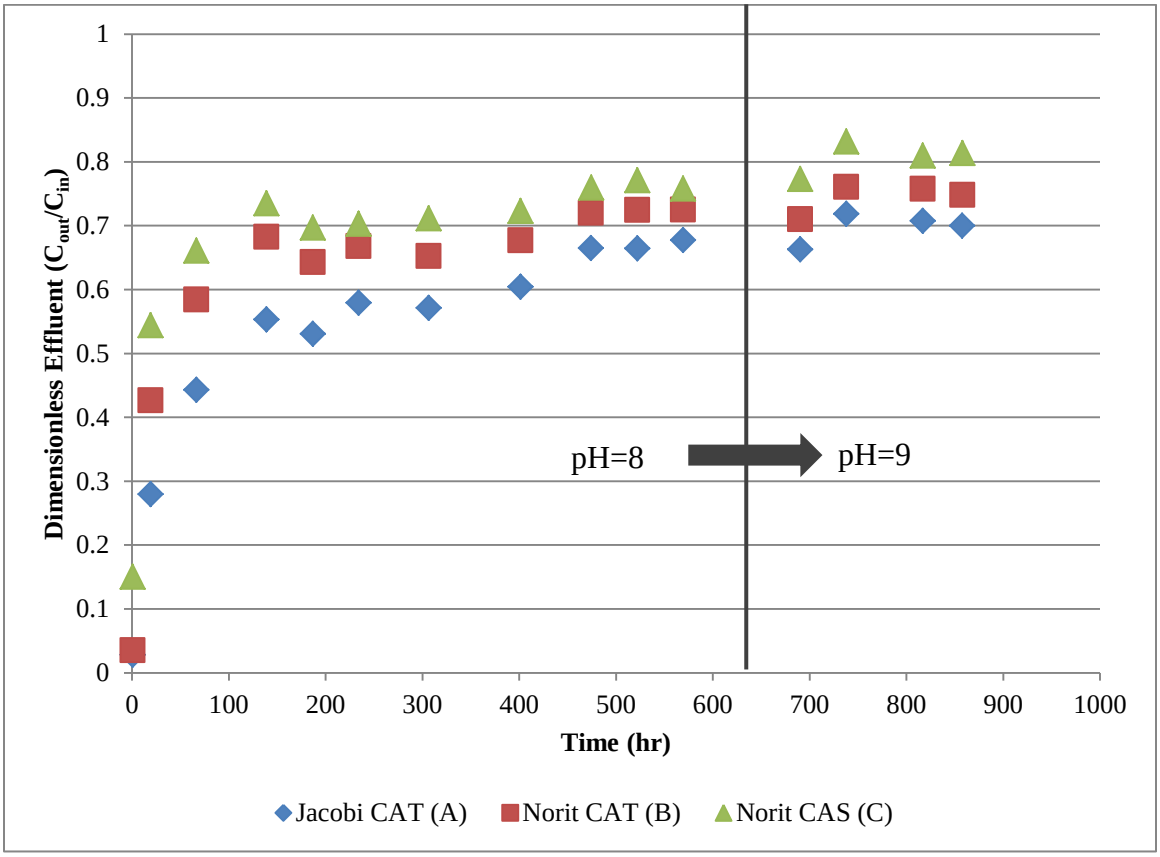


Figure 4-1. Monochloramine dimensionless effluent concentration versus time profile for three GAC samples with 0.25-minute empty bed contact time.

Figure 4-1 clearly shows that all three GAC samples reached a steady state value following a period of higher removal. These results are consistent with previous research (Kim & Snoeyink, 1980b; Fairey et al., 2006). In these 1-cm bed depth experiments, the steady state effluent concentration was attained in approximately 500 hours, which is exactly half the time that Fairey et al. (2006) reported for their 2-cm bed depth columns. The vertical black line denotes a shift in the influent pH from 8 to 9 that occurred at the 690 hour mark. Upon the shift in pH, effluent concentrations rose and a new steady state value was obtained. Figures 4-2 and 4-3 present identical information as Figure 4-1, but at the 0.5- and 0.75-minute empty bed contact time, respectively.

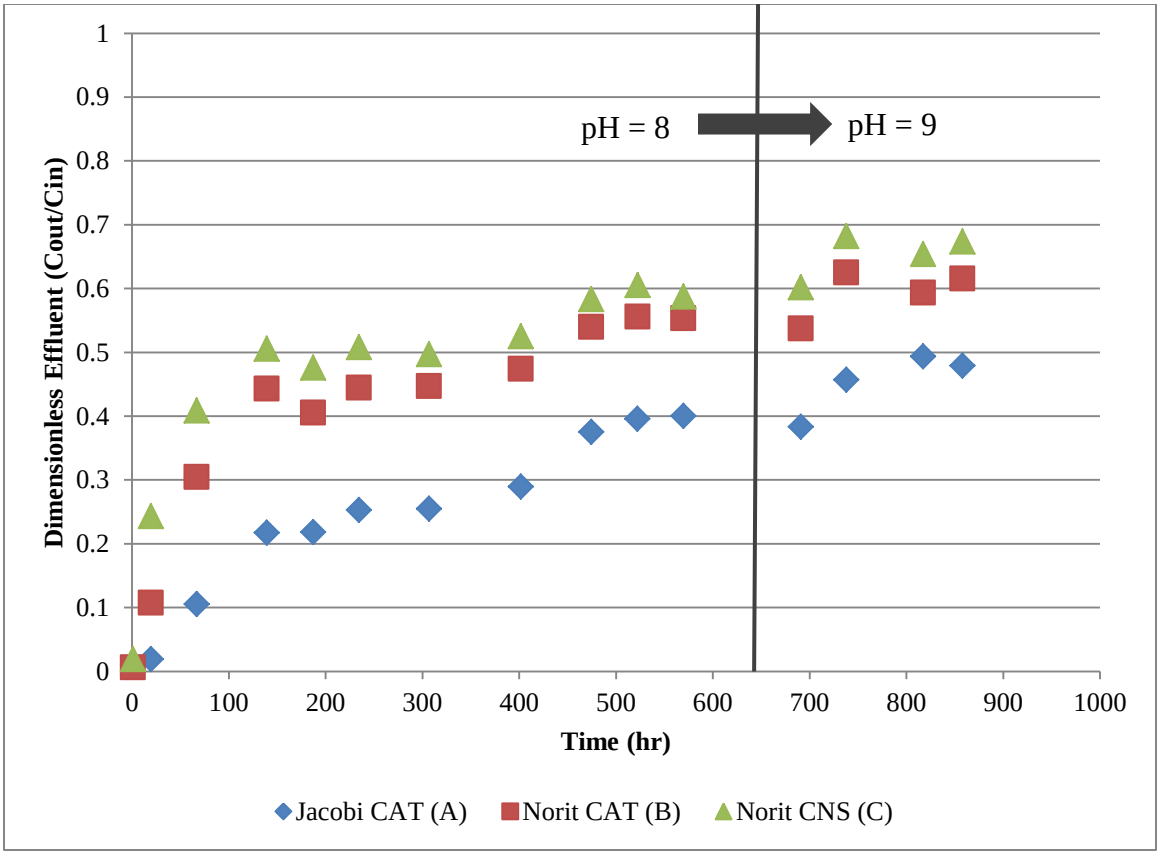


Figure 4-2. Monochloramine dimensionless effluent concentration versus time profile for three GAC samples with 0.5 minute empty bed contact time.

In figure 4-2, steady state is again reached. After the pH shift, steady state is again approached. As expected, the dimensionless effluent monochloramine concentrations are lower than with the 0.25-minute EBCT, as more GAC is allowed to react and more contact time is available for catalysis. Similar trends are noticed from Figure 4-3. Steady state is approached at both pH 8.0 and 9.0. Furthermore, effluent concentrations are the lowest, as the larger mass of GAC with longer contact time provides the best monochloramine destruction.

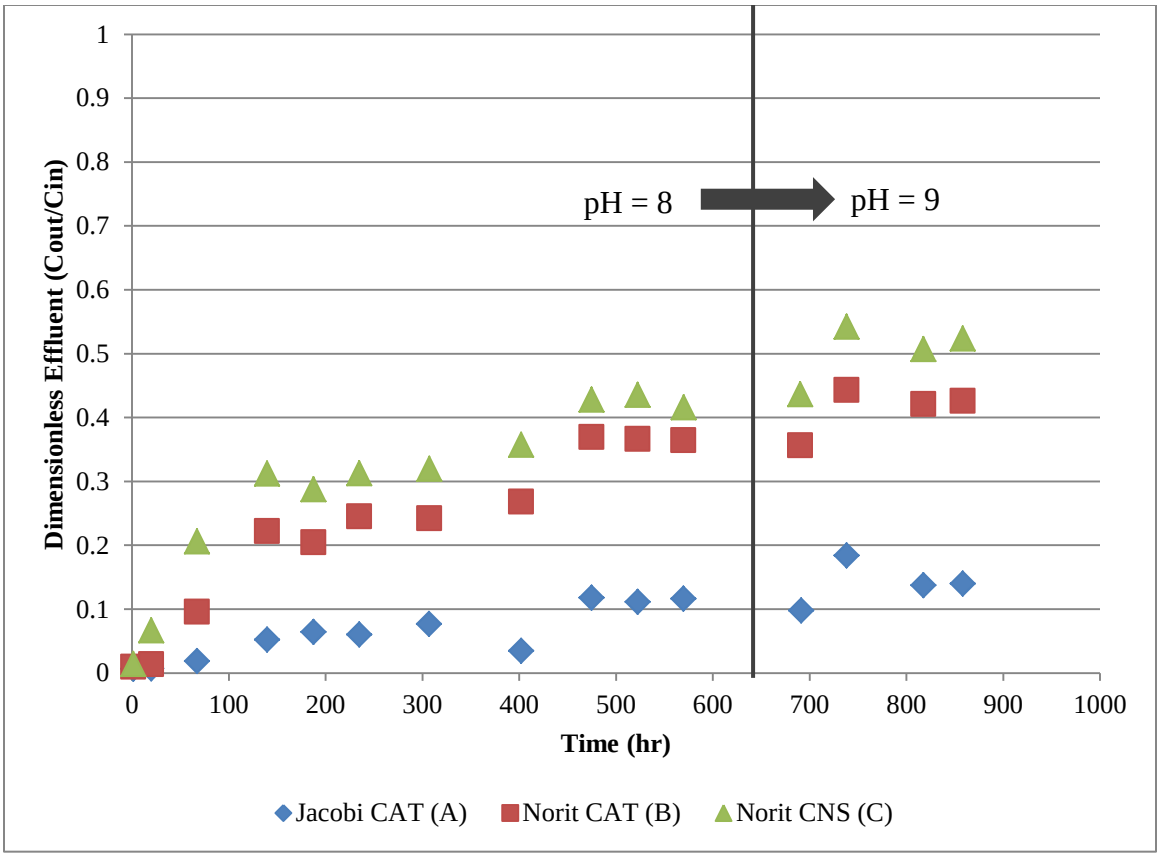


Figure 4-3. Monochloramine dimensionless effluent concentration versus time profile for three GAC samples with 0.75 minute empty bed contact time.

From the combination of Figures 4-1 through 4-3, it is clearly noticeable that Jacobi CAT is the most efficient of the GACs tested, with the lowest dimensionless effluent monochloramine concentration. This performance is followed by Norit CAT and finally, Norit CNS. Furthermore, when viewing Figures 4-1 through 4-3, it appears that both Norit CAT and Norit CNS perform very similarly at each EBCT. As the contact time increases, the margin by which Jacobi CAT outperforms the other two activated carbons increases; both Norit carbons are nearly identical, with Norit CAT displaying slightly better monochloramine removal at all conditions tested. Since these two Norit GACs have different raw materials and activation methods, these results could be pure coincidence. In summary, the breakthrough curves show distinct differences between each of the activated carbons tested.

Using results from the FBR experiments, steady state dimensionless effluent monochloramine concentrations were averaged for all points deemed steady state to compute an average dimensionless effluent concentration for each GAC and condition. Steady state was defined as the time when two subsequent sampling points were within 0.03 C/C_0 of one another for each given condition. Using this value, steady state removal efficiencies were calculated by subtracting the dimensionless effluent concentration fraction from 1 and multiplying by 100 %. A summary of the results presented in Table 4-1 indicates that removal efficiency varies substantially with GAC type.

Table 4-1. Summary of dimensionless effluent monochloramine concentration and steady state removal efficiency for all conditions tested in FBR studies.

		0.25-Min EBCT		0.5-Min EBCT		0.75-Min EBCT	
	Carbon Description	**Css/Cin**	**SS Removal Eff**	**Css/Cin**	**SS Removal Eff**	**Css/Cin**	**SS Removal Eff**
pH=8	Jacobi CAT	0.669	33.1%	0.390	61.0%	0.115	88.5%
	Norit CAT	0.723	27.7%	0.549	45.1%	0.367	63.3%
	Norit CNS	0.763	23.7%	0.592	40.8%	0.426	57.4%
pH=9	Jacobi CAT	0.704	29.6%	0.486	51.4%	0.139	86.1%
	Norit CAT	0.753	24.7%	0.604	39.6%	0.423	57.7%
	Norit CNS	0.812	18.8%	0.664	33.6%	0.515	48.5%

From Table 4-1, quantified results provide insight into the performance of each activated carbon, and highlight trends in the FBR results. First, removal efficiency is improved as empty bed contact time is increased. To graphically depict the effect of EBCT on each GAC, graphs were created. Figure 4-4 shows removal efficiency as a function of EBCT for pH 8 while Figure 4-5 corresponds to pH 9. From Figures 4-4 and 4-5, a near linear relationship between EBCT and steady state removal efficiency is observed. This result is consistent with previous work at similar EBCTs (Fairey, 2006).

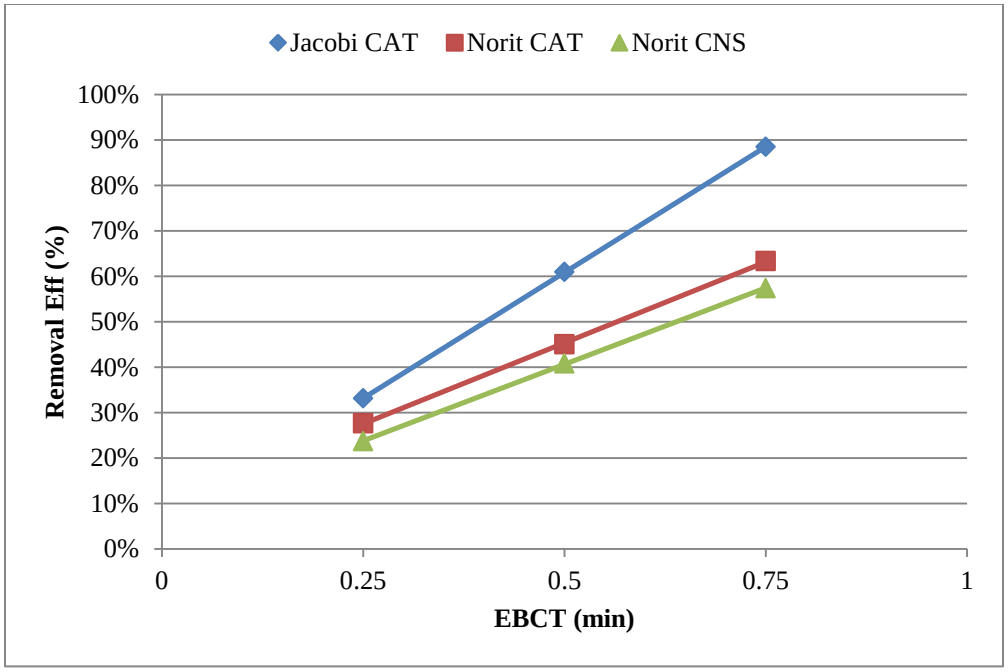


Figure 4-4. Monochloramine removal efficiency for each GAC tested as a function of empty bed contact time at pH 8.

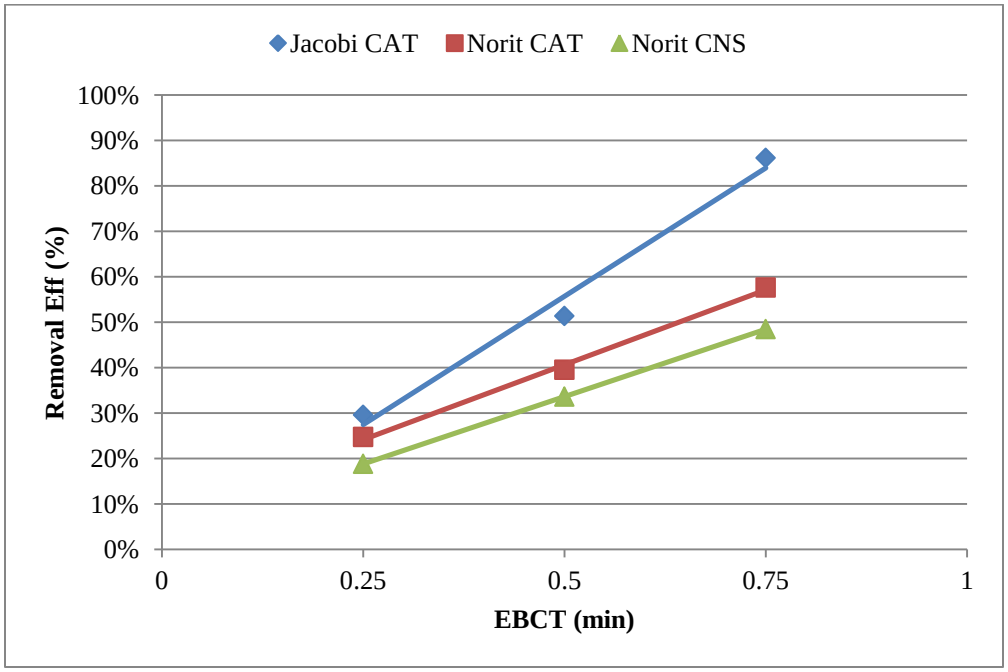


Figure 4-5. Monochloramine removal efficiency for each GAC tested as a function of empty bed contact time at pH 9.

Furthermore, the quantitative ranking of each activated carbon is apparent from Table 4-1. Experiments with Jacobi CAT at pH 8 yielded a steady state monochloramine removal efficiency of nearly 90 % for a 0.75-min EBCT. This is compared to Norit CAT displaying slightly more than 60% removal, while Norit CNS showed slightly less than 60% removal. Finally, the effects of pH are evident from the results. Focusing on Norit CNS, removal efficiency dropped from 57.4 % at pH 8 to 48.5 % when the pH was raised to 9. Two possible causes of this trend in increased removal efficiency with decreasing pH have been hypothesized in the literature. Because the speciation of chloramines is highly pH dependent, monochloramine is slightly more stable at higher pH values (9 versus 8). Increased stability could leady to slower catalytic destruction of the compound. Fairey (2006) evaluated this possibility and concluded that it is unlikely that monochloramine speciation alone would yield the extent of reduction in removal efficiency because dichloramine (less stable) comprised less than 1% of the chloramine species at all pH values tested. However, during FTIR analysis (See section 4.3.2.), Fairey (2006) identified several functional groups with pKa's in the pH 8 to 9 range which suggests that GAC acid/base character could further account for pH effects.

Although the results of Fairey et al. (2006) evaluated activated carbons at longer EBCTs (0.5, 1.0, and 1.5 min) and used two different source waters (organic free synthetic water and raw filtered Lake Austin water), comparisons between the activated carbons used in this work and Fairey's research is possible. The results of this previous research at the 0.5-min EBCT using Lake Austin water at pH 8 were compared with FBR results from this research at the 0.5-min EBCT using tap water at pH 8. Fairey reported the TOC of Lake Austin water to be between 2.5 to 3.5 mg/L, which is in the range of reported City of Austin tap water used in this research; in fact, Lake Austin water is the

sole source for City of Austin drinking water. However, drinking water plants in the city of Austin remove 20-40 percent of TOC from raw water before it reaches the end users (Austin Water Utility, 2012). It is important to understand differences in organic carbon concentrations before comparing results. Table 4-2 presents a summary of dimensionless effluent monochloramine concentrations and steady state monochloramine removal efficiencies from this work along with the results from Fairey et al. (2006).

Table 4-2. Comparison between steady state monochloramine concentration and removal efficiency for FBR studies and results from Fairey's (2006) FBR studies.

		0.5 Min EBCT	
	Carbon Description	**Css/Cin**	**SS Removal Eff**
pH=8	Jacobi CAT	0.390	61.0%
	Norit CAT	0.549	45.1%
	Norit CNS	0.592	40.8%
	F400*	0.760	24.0%
	F600*	0.700	30.0%
	Centaur*	0.460	54.0%
	AGC-MG*	0.750	25.0%
	Aquaguard*	0.640	36.0%

*Experiments run using Lake Austin Water, which could have 20-40% higher TOC values.

In this comparison, the advance of activated carbon technologies can be seen. F400 and F600 are standard activated carbons, and exhibit much less monochloramine reduction than any other carbons. Centaur and Aquaguard were designed specifically for monochloramine removal and were advertised with catalytic activation strategies. They

are clearly better performers. However, only Centaur, (the top performing activated carbon in Fairey's work) accomplishes better removal than Norit CAT and CNS. Jacobi CAT activated carbon outperforms all carbons tested in this research, as well as all carbons tested in previous research. The impact of natural organic matter can be seen in results from Fairey (2006). The removal of Centaur GAC was 54 % in Lake Austin water while increasing slightly to 60% in an organic free solution. Aquaguard carbon was strongly affected by organics, as its monochloramine removal in Lake Austin Water and the organic free solution was 36 and 84%, respectively. It is apparent that natural organic matter alters GAC performance to varying degrees, based on carbon identity.

For this research, it is important to realize that the amount of organic matter in the City of Austin tap water will reduce the performance of the GACs relative to organic free water. Point of use filters using tap water can experience a wide variety of influent water conditions, depending on the geographical region and treatment scheme of the municipality of interest. Therefore, results from experiments could vary depending on the characteristics of the influent water stream.

4.3. ACTIVATED CARBON CHARACTERIZATION

4.3.1. Physical Characterizations of GAC

Nitrogen gas adsorption isotherms were obtained for each of the GAC samples using methods outline in section 3.4.1. Figure 4-6 depicts the nitrogen gas adsorption/desorption isotherm for Jacobi CAT. The isotherms for Norit CAT and Norit CNS can be seen in Appendix B.

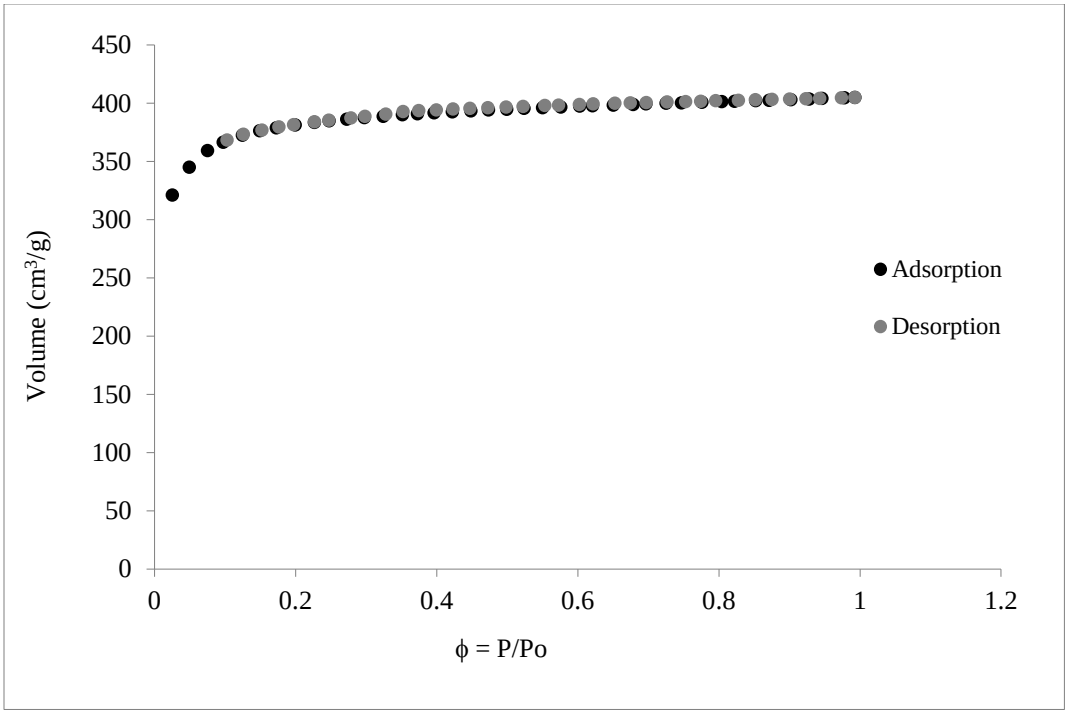


Figure 4-6. Nitrogen gas adsorption/desorption isotherm for Jacobi CAT.

From Figure 4-6 and by IUPAC classification, the isotherm of Jacobi CAT was classified as Type 1. This isotherm type provides insight into the pore structure. Type 1 isotherms are indicative of microporous solids. The shape of the curve shows that adsorption is limited to completion of single monolayer as pores are completely filled. Further, the steep gradient towards the beginning of the curve indicates narrower micropores are the major type of pore contained within the GAC sample. The BET method was used to calculate specific surface area of each of the activated carbons. A BET graph for Jacobi CAT is presented in Figure 4-7 below, highlighting the linear region of the curve that was used for the analysis. Similar figures for the other two GAC samples are presented in Appendix B. Both Norit CAT and Norit CNS also displayed Type 1 isotherms.

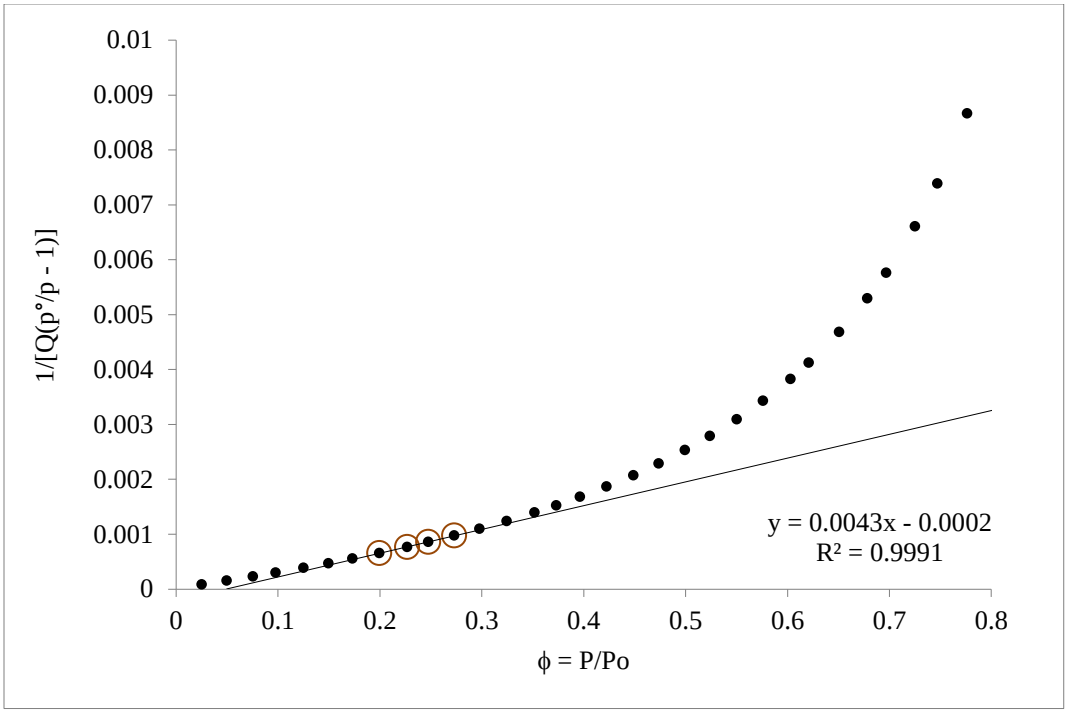


Figure 4-7. BET plot for Jacobi CAT.

Using the BET method, specific surface area was calculated. Total pore volume, micropore volume, and mesopore volume was calculated for each sample using the methods adapted from Gregg & Sing (1982) and Fairey et al. (2006) that were previously described. Furthermore, the percent of total pore volume comprised of micropores was calculated to give insight into the pore size distribution of each GAC. Table 4-3 summarizes the physical characteristics obtained in this research.

Table 4-3. Summary of physical properties of GAC samples considered.

		Pore Volume (cm^3/g)			
GAC	**Specific Surface Area (m^2/g)**	**Total**	**Micro-**	**Meso-**	**Percent Micropores**
Jacobi CAT	1056	0.625	0.618	0.007	98.9%
Norit CAT	1106	0.627	0.502	0.125	80.1%
Norit CNS	821	0.403	0.385	0.018	95.6%

The specific surface area of Jacobi CAT was found to be 1056 m^2/g. A look at the manufacturer product sheet provides a specific surface area of 1060 m^2/g (Jacobi, 2007), indicating excellent correlation between claimed and experimental data. Furthermore, the interpretation given by the Type 1 isotherm is confirmed quantitatively. Nearly 99 % of the pore volume contained in a Jacobi CAT particle is classified as microporous, meaning they are less than 2 nm in diameter. This pore distribution can provide great understanding of the performance of each GAC. Since the tap water used in the FBR experiments contained natural organic matter, it is conceivable that the large amount of micropores were not accessible to the NOM. This could explain the exceptional performance of the Jacobi CAT carbon in FBR studies, as only about 1 % of the pores were larger than 2 nm, and thus susceptible to blockage from NOM. The work of Fairey (2006) confirmed that size distributions of pores directly correlated to the portion of active sites that could be blocked or constricted due to infiltration by organic matter. Norit CAT, the other claimed catalytic activated carbon, has comparable surface areas as Jacobi CAT; however, it lacks the amount of micropores. This result could explain why Jacobi CAT outperformed Norit CAT in the FBR studies. Furthermore, looking at the work of Fairey (2006), similar trends were present. The top performing GAC in natural

waters in Fairey's research, Centaur, had the highest percentage of micropores tested at 94.4%. Comparing to this research, Centaur had a total micropore volume of 0.43 cm^3/g, compared to 0.618 cm^3/g shown by Jacobi CAT. These results seem to indicate that Jacobi CAT has a more favorable micropore structure, compared to other GACs tested.

4.3.2. Chemical Characterizations of GAC

The chemical properties of the surface of activated carbon particles were evaluated in an effort to correlate catalytic performance. In theory, the GAC-monochloramine catalysis reaction is controlled, at least in part, by the surface chemistry of the GAC. To characterize the acid and base properties of each of the granular activated carbons, Boehm Titrations were performed. An example set of titration curves to determine total acidity and total basicity for the Norit CAT GAC sample are shown in Figures 4-8 and 4-9, respectively. Titration curves for all other samples are located in Appendix C.

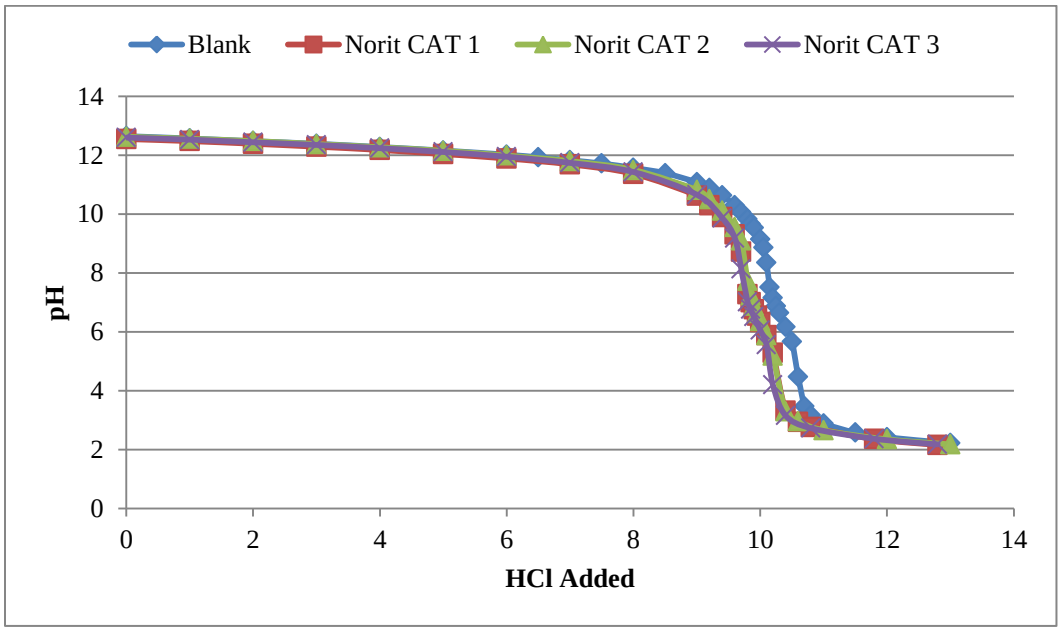


Figure 4-8. NaOH uptake titration curve for Norit CAT to determine total acidity.

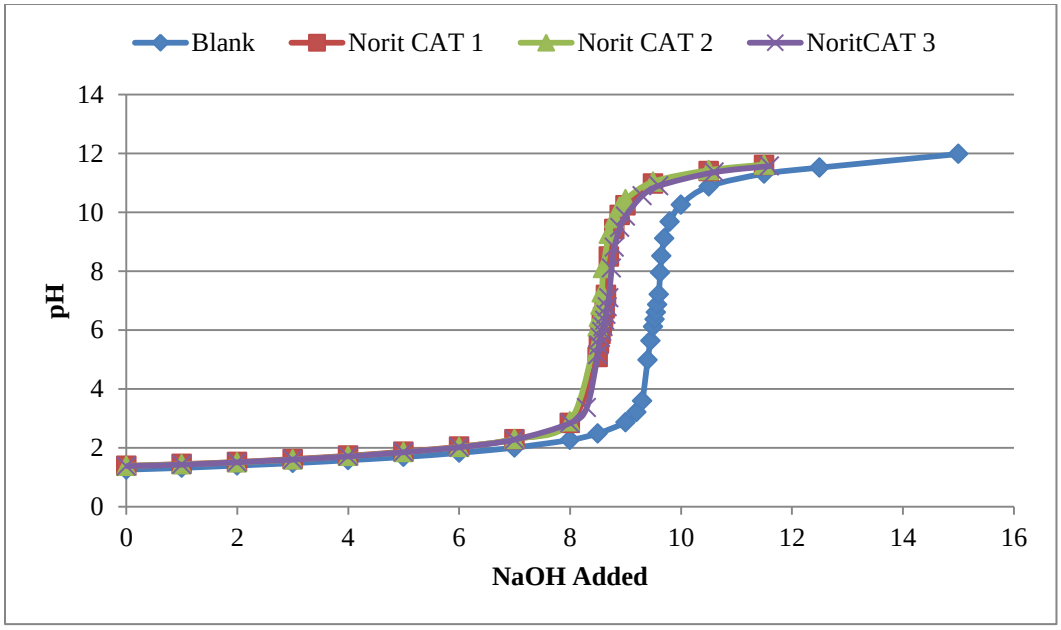


Figure 4-9. HCl uptake titration curve for Norit CAT to determine total basicity.

These figures include the blank titration curve and three curves representing supernatant from the triplicate samples that were equilibrated with the GAC, in this case Norit CAT. The differences in milliequivalents of acid or based to reach pH 7 were then converted to milliequivalents of acid or base that was taken up by the functional groups on the GAC surface. NaOH uptake represents total acidity while HCl uptake represents total basicity. Since a known mass of sample was equilibrated with acid or base during the titration, acidity and basicity are reported in units of milliequivalents per gram (meq/g). However, another useful representation of the results is seen when the values are normalized on a column basis. This was performed by multiplying the acidity/basicity by the packed bed density. The resulting units are milliequivalents per cubic centimeter (meq/cm^3). Total acidity and basicity of each activated carbon sample are presented in both units in Table 4-4.

Table 4-4. Summary of total acidity and total basicity for each GAC sample on the basis of mass and column volume.

	Acidity		Basicity	
	Average NaOH Uptake (meq/g)	**Average NaOH Uptake (meq/cm^3)**	**Average HCl Uptake (meq/g)**	**Average HCl Uptake (meq/cm^3)**
Jacobi CAT	0.34*	0.17	0.60	0.29
Norit CAT	0.35*	0.13	0.91	0.34
Norit CNS	0.36*	0.21	0.38	0.22

*Not statistically different at 95% confidence limit.

As shown in Table 4-4, Norit CNS exhibited the highest acidity and lowest basicity. Previous research has shown that lower acidity leads to increased catalytic properties; however, all of the GACs examined in this work have similar acidity values. Furthermore, conflicting results have been show with regard to basicity. Some authors have shown increased catalytic activity with increasing basicity. This claim is supported by Norit CNS results compared to Norit CNS. However, the trends in basicity of Jacobi CAT and Norit CAT do not correlate with their relative performance, suggesting that neither acidity nor basicity measurements can be used to distinguish performance. These results suggest that although the total acidity and basicity of the surface functional groups on a GAC may be one important factor, other characteristics control the relative performance with regard to monochloramine catalysis for the GACs tested. While Norit CAT appears to have the highest abundance of surface groups, its pore structure may not be as accessible as the active sites on Jacobi CAT or the particular composition of the sites may not be as reactive to monochloramine. If monochloramine cannot freely enter the active site of the GAC surface, it cannot react and thus, removal is not stimulated as

efficiently. If particular types of functional groups impart similar acidity or basicity in the Boehm titration, but are more or less reactive to monochloramine, then comparisons among the results from different activated carbons may not correlate with performance.

While the Boehm titration method was enacted to determine raw acidity and basicity, little was known of the identity of the surface functional groups. Thus, FTIR spectroscopy was used to assess qualitative aspects of the GAC surface. Using methods established in Chapter 3, FTIR was performed on each of the three activated carbon samples. The entire scan showed a strong band between 3700 and 3000 cm^{-1} and many bands with varying intensity between 2000 and 700 cm^{-1}. These results are consistent with previous research, including Stuart et al. (2004) and more recently, Fairey et al. (2006). To get a better view of the areas of interest, the FTIR spectrum was focused on the area between 2000 and 700 cm^{-1} for each of the GAC samples. A plot containing this region with each of the three GAC samples overlaid is presented in Figure 4-10.

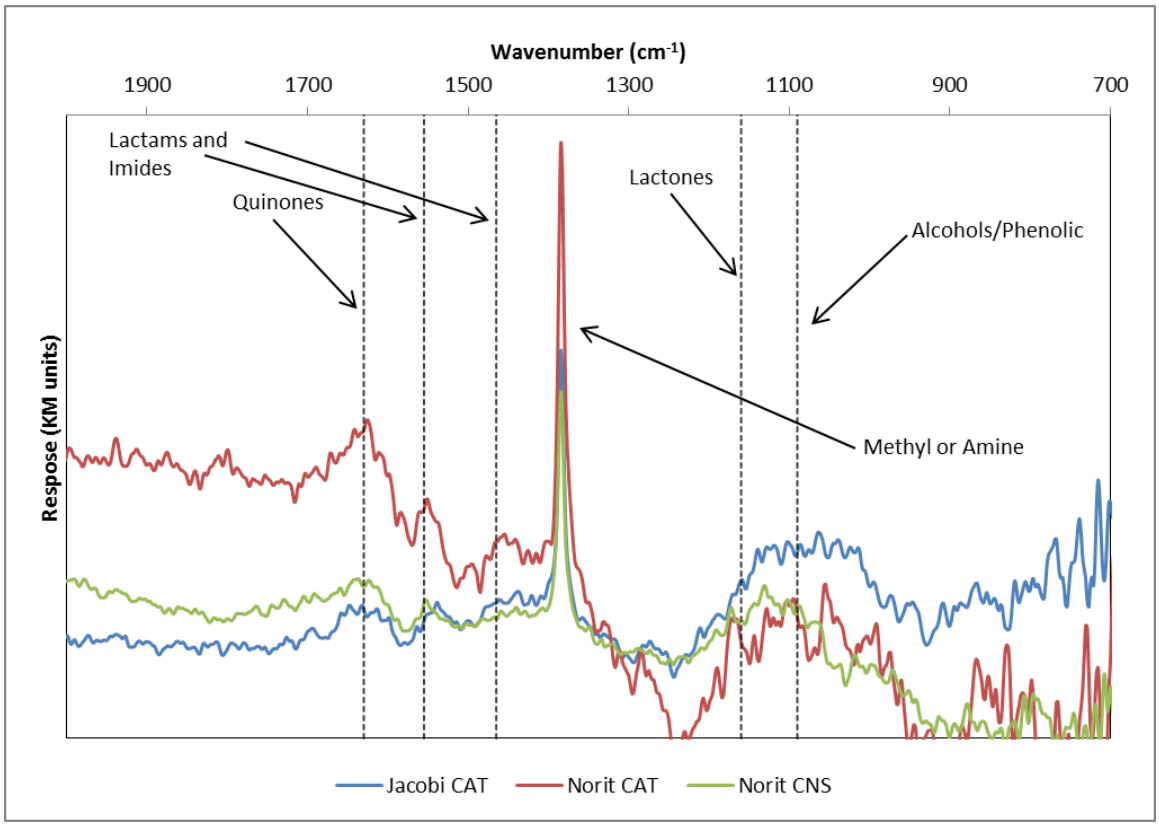


Figure 4-10. FTIR spectra for each GAC tested in the 2000 cm^{-1} to 700 cm^{-1} region.

Individual spectra are shown in Appendix C. Previous research was utilized in an effort to help identify the various peaks that were present in the FTIR results. Vertical dashed lines shown in Figure 4-10 depict the functional group most likely associated with the corresponding peak. Similar peaks are evident in each of the GAC spectra. The peak located around 1650 cm^{-1} is associated with quinones, which are essentially any class of aromatic compounds having two carbonyl functional groups in the same six-membered ring (Marsh, 2006). The two peaks at 1550 and 1470 cm^{-1} are due to C=C stretching and were assigned to imides, amides, and lactams (Fairey et al., 2006). Lactams are a blend of a lactone and an amide. The very large, sharp peak at 1385 cm^{-1} is most likely due to methyl or amine groups. The peak at 1170 cm^{-1} is attributed to C-O stretching vibrations,

which has been shown to be supported by the formation of lactonic structures (Ishizaki & Martin, 1981). Finally, the large broad peak at around 1100 cm^{-1} is consistent with alcohols or phenolic functional groups.

The identity of certain function groups provides much insight into the GAC-monochloramine catalytic reactions that are considered in this research. Previous research has elucidated lactones as powerful monochloramine reductants. Ascorbic acid is classified as a lactone and has been used for many medical and analytical purposes to dechlorinate water. Bedner (2004) has shown that this compound is effective at reducing both free chlorine and monochloramine. Additionally, the chemical properties of imides shown to exist on all three GAC samples further justifies the large pH dependency of monochloramine destruction that was evident in Phase 1. Imides have pKa's between 8 and 10. The shift from pH 8 to 9 that was performed in the FBR studies could have caused deprotonation of the imide groups, which could lead to fewer acidic surface groups that could participate in the reactions; this could explain the decreased monochloramine removal seen at higher pH values.

4.3.3. Correlating Physical and Chemical Properties to Performance

As several trends were evident when analyzing the various properties of the GACs tested, it was important to correlate these features to steady state performance. To accomplish this, various characteristics of each GAC were plotted versus steady state monochloramine removal efficiency. Each of the scenarios tested in the fixed bed reactor study were plotted, and a linear regression analysis was performed. The coefficient of determination (R^2) was taken as a general indicator of the goodness of fit performed by the regression. A sample of an analysis graph is shown in Figure 4-11 to determine the correlation between micropore volume and GAC performance in the FBR studies.

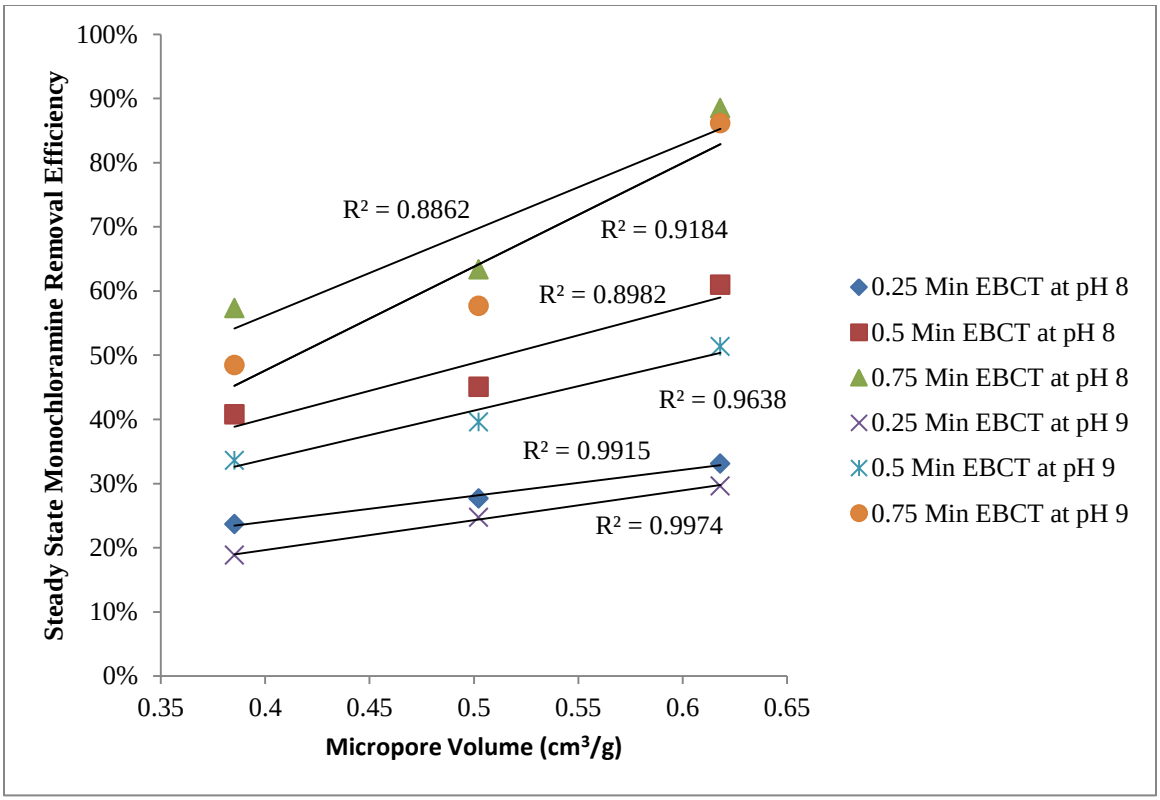


Figure 4-11. Steady state monochloramine removal efficiency versus micropore volume for all GACs tested.

Additional plots used to determine correlations between all physical and chemical properties evaluated in Phase 2 of this research are shown in Appendix D. The coefficient of determination was tabulated to summarize relationships. This can be viewed in Table 4-5 below. An R^2 value of 0.7 or greater was taken as being a significant correlation. Again, acidity was not analyzed because values were statistically identical.

Table 4-5. Coefficient of determination (R^2) for each of the physical/chemical properties versus steady state removal efficiency.

	Coefficient of Determination (R^2)						
Physical/Chemical Characteristic	**0.25 Min EBCT pH 8**	**0.5 Min EBCT pH 8**	**0.75 Min EBCT pH 8**	**0.25 Min EBCT pH 9**	**0.5 Min EBCT pH 9**	**0.75 Min EBCT pH 9**	**Average**
Micropore Volume	0.992	0.898	0.886	0.997	0.964	0.918	0.943
BET Surface Area	0.507	0.282	0.265	0.649	0.409	0.314	0.404
Total Pore Volume	0.662	0.432	0.413	0.789	0.565	0.467	0.555
Acidity (mass)	-	-	-	-	-	-	-
Basicity (mass)	0.109	0.011	0.007	0.213	0.055	0.019	0.069

From Table 4-5, the relationships between performance and micropore volume seem compelling. Thus, statistical analysis has upheld previous research and hypotheses of this research. The microporous nature of the carbon allows the active sites to be accessible by only small molecules, such as the target monochloramine.

4.4. MODELING

The use of the monochloramine catalysis (MCAT) model developed by Kim (1977) to simulate steady state effluent concentration in full scale GAC columns required two steps. First, the model was calibrated using FBR results. Next, parameters were scaled to those found in a full size system, and the model was executed to simulate performance.

4.4.1. Model Calibration

The MCAT model was calibrated with the FBR results that were presented in Table 4-1. Other parameters that were specified in the model calibrations are shown in Table 4-6 and 4-7. Table 4-6 displays the column characteristics and assumed constants

while Table 4-7 highlights the GAC pore volume and packed bed density that were obtained from the physical characterizations outline in Section 4.3.1.

Table 4-6. Column characteristics and assumed constants used for model calibration.

Parameter	Model Symbol	Units	Value
Bed diameter	dia	cm	1
Bed length	xb	cm	2.55, 5.1, 7.65
Flow rate	flow	mL/min	8
Influent Concentration	cinf	mg/L as Cl_2	1.5
Geometric mean GAC diameter	dpart	cm	0.035
Bed porosity	xporo	-	0.30
Effective solute diffusivity	dc	cm^2/min	0.0009*
Axial dispersion coefficient	da	cm^2/min	3*
Mass transfer coefficient	xk	cm/min	1000*
* Source: Kim (1977)			

Table 4-7. GAC physical characteristics used for model calibration.

Parameter (Model Input)	Units	Jacobi CAT	Norit CAT	Norit CNS
Pore Volume (xpv)	cm^3/g	0.625	0.627	0.403
Adsorbent Apparent Density (ro)	g/cm^3	0.699	0.535	0.837
Packed-bed density (wconc)	g/cm^3	0.489	0.374	0.586

The MCAT model was calibrated for each of the GAC samples (Jacobi CAT, Norit CAT, Norit CNS) in each of the two influent water conditions (pH 8.0 and 9.0). Figures 4-12 through 4-14 show the MCAT model calibration fits for pH 8.0 and 9.0 for Jacobi CAT, Norit CAT, and Norit CNS, respectively.

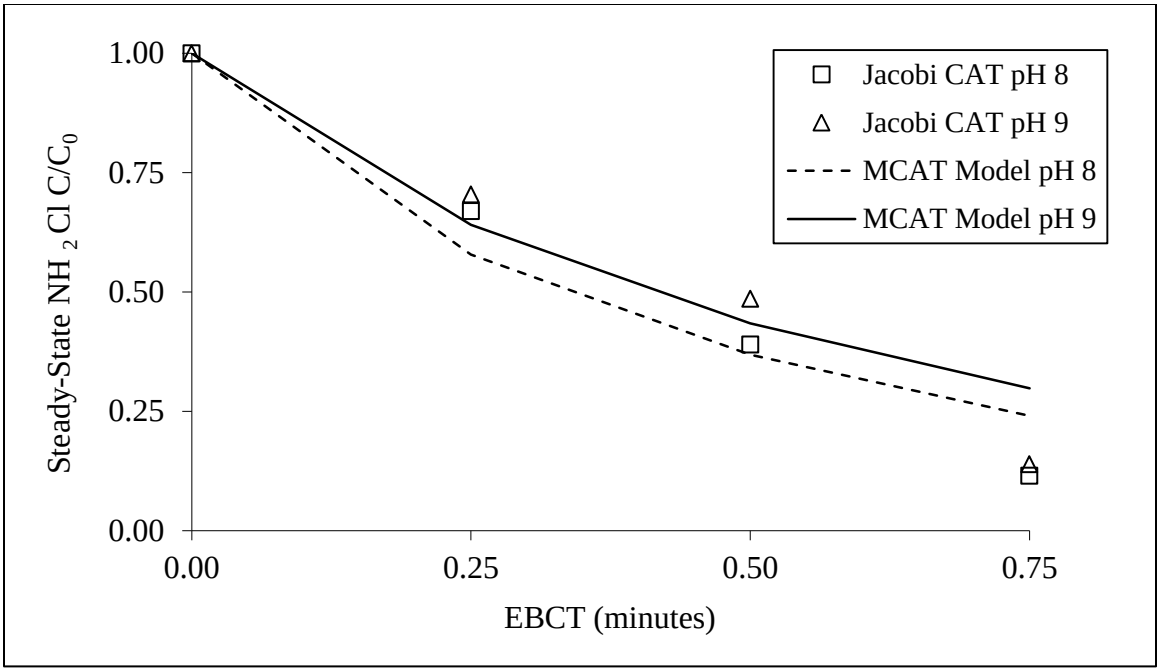


Figure 4-12. Monochloramine catalysis (MCAT) model calibration of steady state data from FBR experiments with 40 X 50 US mesh Jacobi CAT at pH 8.0 and 9.0.

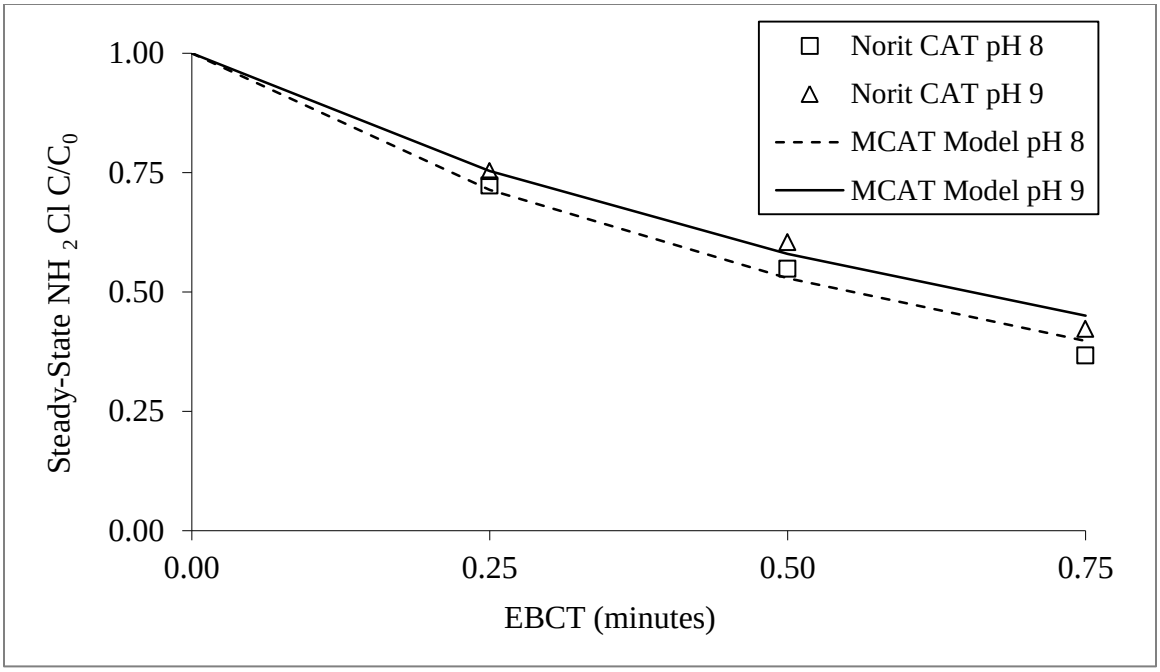


Figure 4-13. Monochloramine catalysis (MCAT) model calibration of steady state data from FBR experiments with 40 X 50 US mesh Norit CAT at pH 8.0 and 9.0.

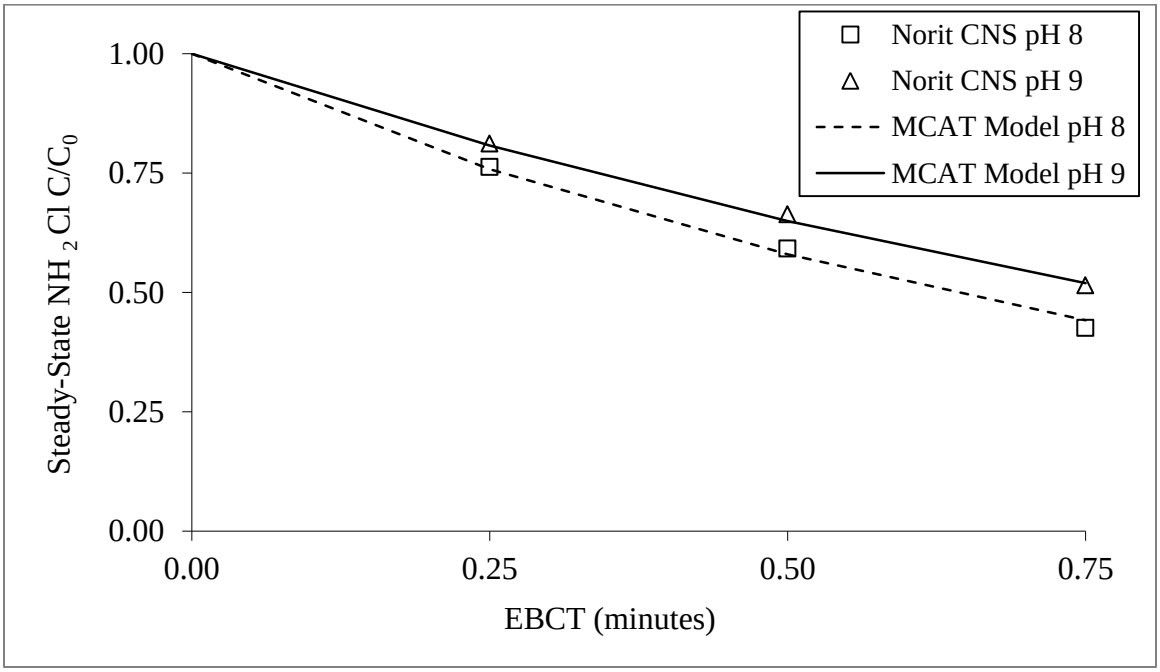


Figure 4-14. Monochloramine catalysis (MCAT) model calibration of steady state data from FBR experiments with 40 X 50 US mesh Norit CNS at pH 8.0 and 9.0.

The values of the best fit model rate constant, f_7, which controls the rate of monochloramine catalysis for each GAC at both influent water conditions are presented in Table 4-8. It is noted that these values do not change as the GAC particle size, or other operational parameters, are varied. The rate constant values obtained in this research are of consistent magnitude with those found in the work of Fairey et al., 2006.

Table 4-8. Values of the fitted model rate constant for each GAC sample at each pH.

	f_7	
GAC	**pH 8**	**pH 9**
Jacobi CAT	0.970	0.621
Norit CAT	0.575	0.397
Norit CNS	0.326	0.171

With the rate constants determined, the MCAT model was calibrated to run simulations of full scale performance.

4.4.2. Model Simulations

Kim (1977) showed that the MCAT model could successfully be utilized for GAC particles between 60 X 80 and 12 X 20 US mesh sizes. Fairey et al. (2006) implemented the model to predict steady state monochloramine concentrations using the US 12 X 40 mesh size. This research employed modeling efforts to predict the 12 X 40 mesh size, as it is the size used in point of use drinking water filters of interest. Table 4-9 displays the column characteristics and assumed constants used for monochloramine simulations in point of use filters. Table 4-10 highlights GAC characteristics input in the MCAT model. It is noted that the rate constant, f_7, does not change for simulations.

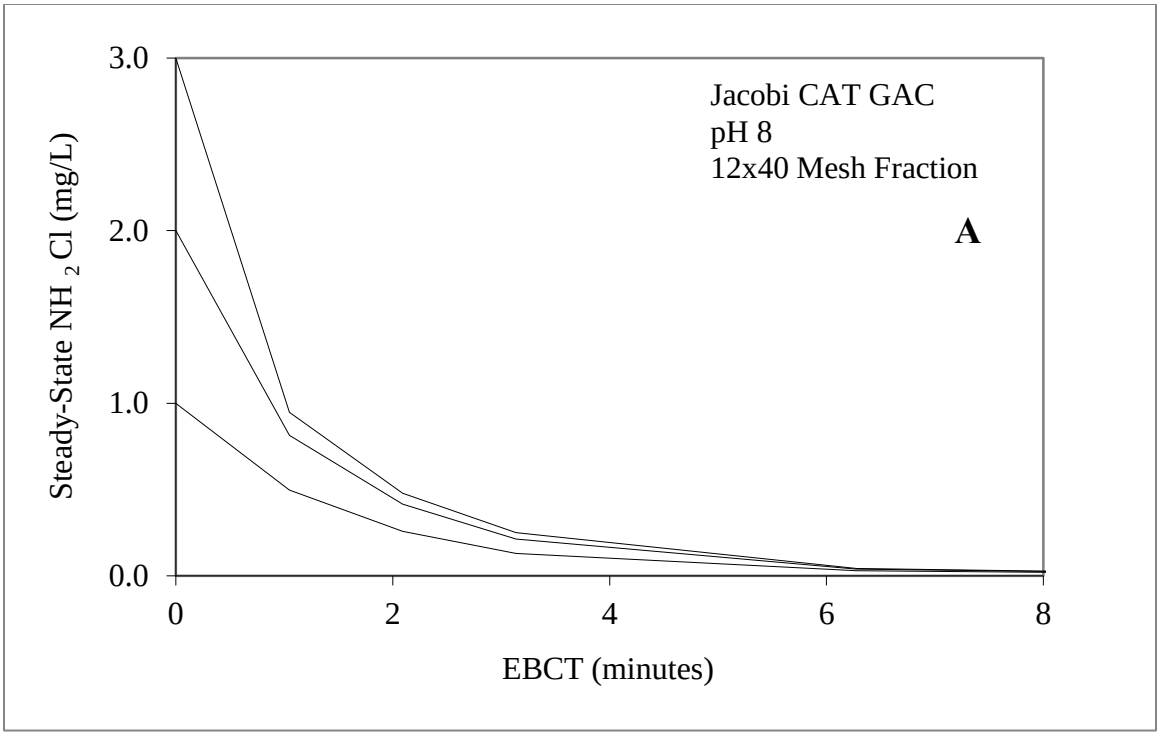
Table 4-9. Column characteristics and assumed constants used for full scale simulation.

Parameter	Model Symbol	Units	Value
Bed diameter	dia	cm	4.73
Bed length	xb	cm	5, 10, 15, 30, 45
Flow rate	flow	mL/min	84
Empty Bed Contact Time	-	min	1.0, 2.1, 3.1, 6.3, 9.4
Influent Concentration	cinf	mg/L as Cl_2	1.0, 2.0, 3.0
Geometric mean GAC diameter	dpart	cm	0.084
Bed porosity	xporo	-	0.40
Effective solute diffusivity	dc	cm^2/min	0.0009*
Axial dispersion coefficient	da	cm^2/min	3*
Mass transfer coefficient	xk	cm/min	1000*
* Source: Kim (1977)			

Table 4-10. GAC physical characteristics used for full scale simulation.

Parameter (Model Input)	Units	Jacobi CAT	Norit CAT	Norit CNS
Pore Volume (xpv)	cm^3/g	0.625	0.627	0.403
Adsorbent Density (ro)	g/cm^3	0.514	0.448	0.63
Packed-bed density (wconc)	g/cm^3	0.437	0.337	0.513

The packed bed density of Jacobi CAT was determined using manufacturer specifications that listed this value. Norit CAT and Norit CNS density was estimated using a full scale column with US 12 X 40 GAC. Figures 4-15 through 4-17 present full scale model simulations for Jacobi CAT, Norit CAT, and Norit CNS, respectively.



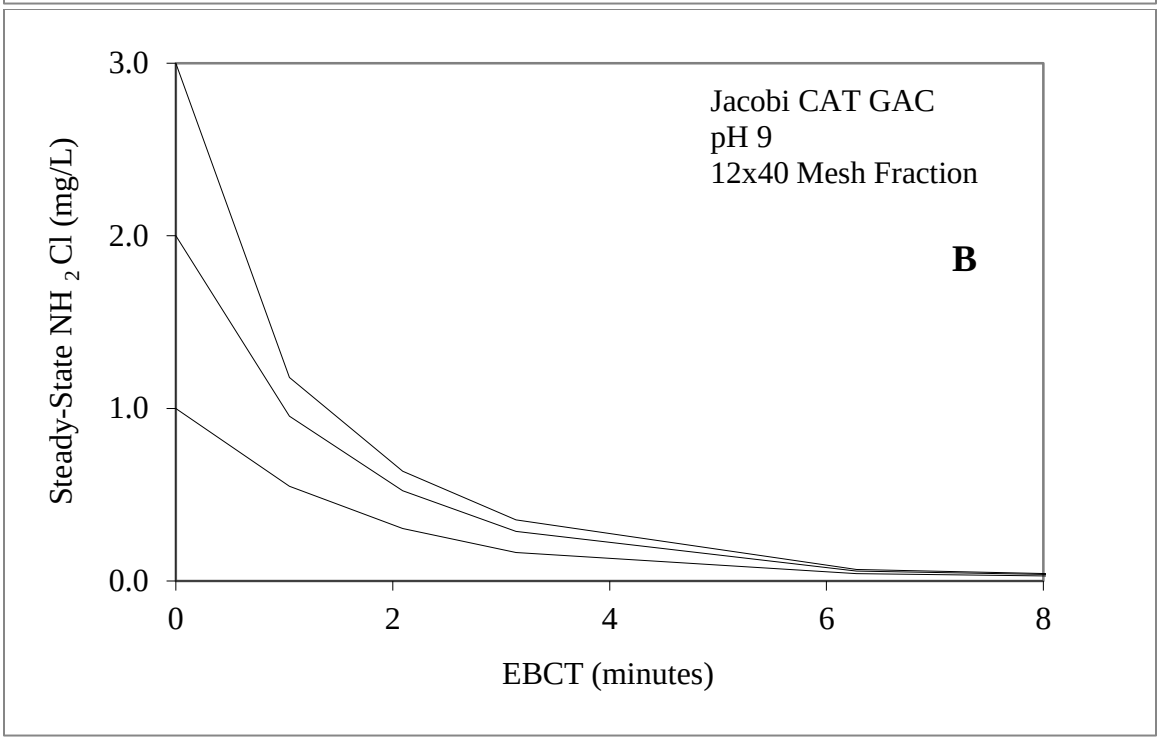


Figure 4-15. Steady state monochloramine effluent concentration profiles of Jacobi CAT in US 12 X 40 mesh size with City of Austin tap water at (A) pH 8 and (B) pH 9.

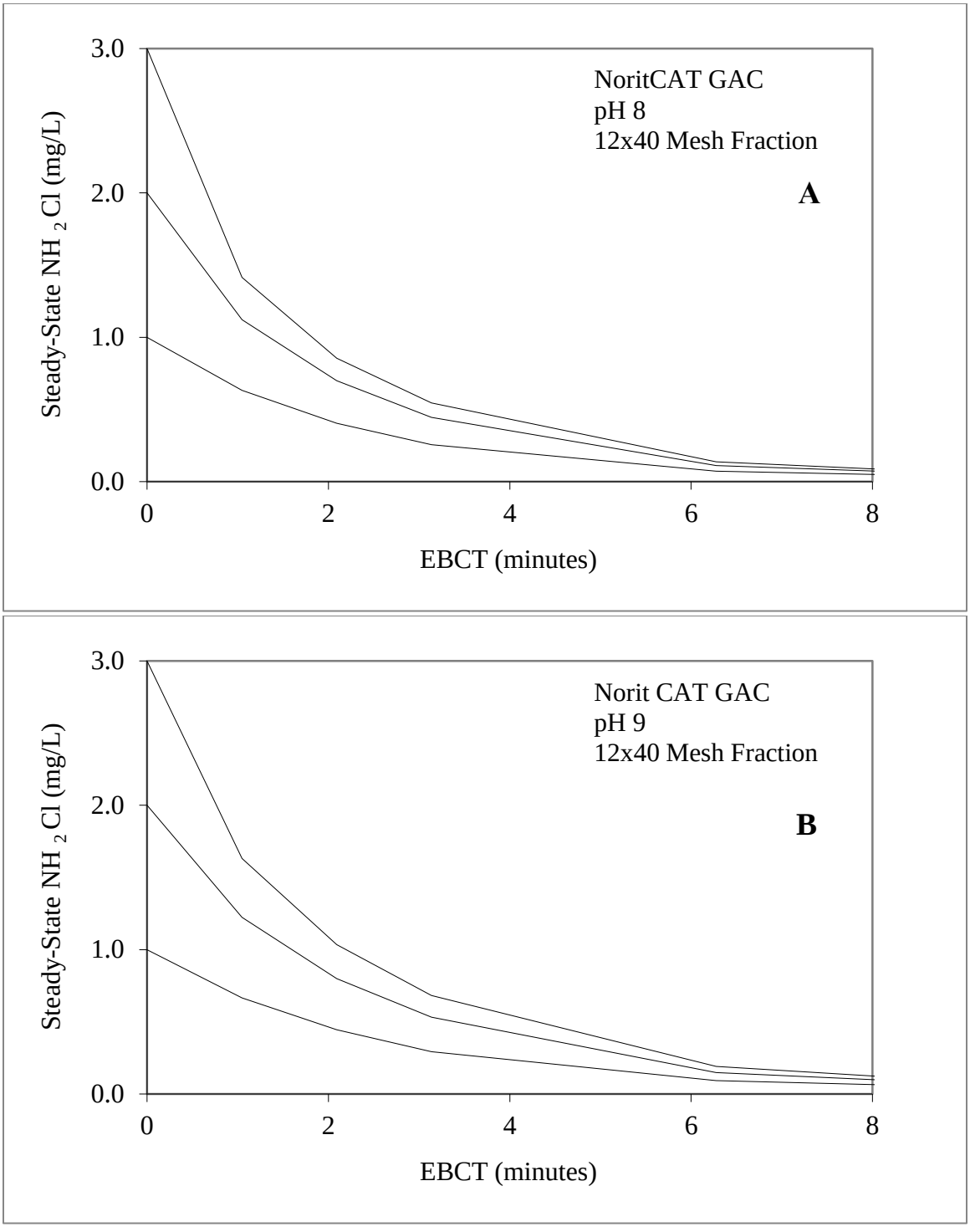


Figure 4-16. Steady state monochloramine effluent concentration profiles of Norit CAT in US 12 X 40 mesh size with City of Austin tap water at (A) pH 8 and (B) pH 9.

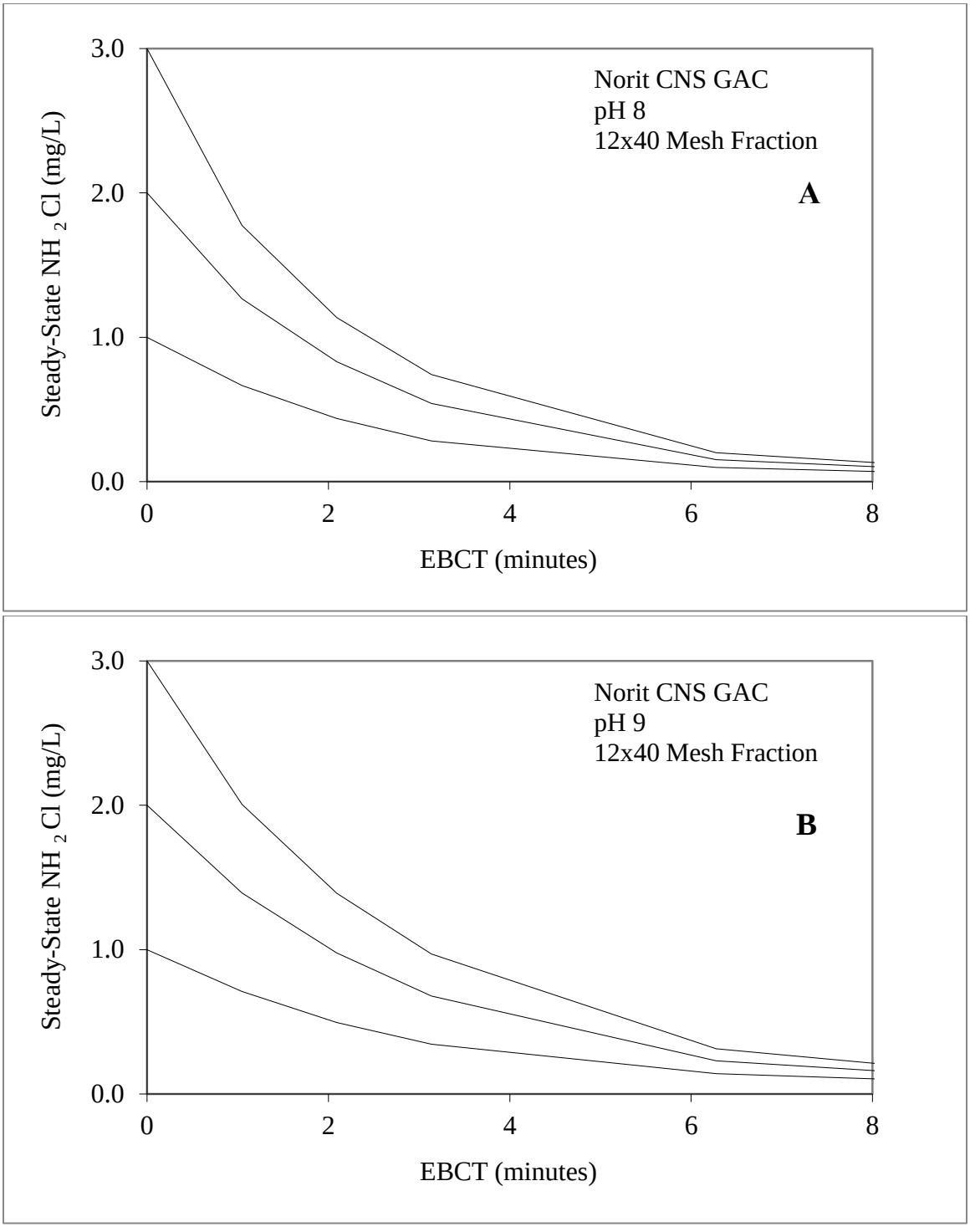


Figure 4-17. Steady state monochloramine effluent concentration profiles of Norit CNS in US 12 X 40 mesh size with City of Austin tap water at (A) pH 8 and (B) pH 9.

Figures 4-15 through 4-17 provide valuable information. The performance of a point of use drinking water filter can be estimated using the influent monochloramine concentration and the empty bed contact time corresponding to the particular filter. For example, at pH 8, a drinking water filter using Jacobi CAT that has an influent concentration of 3 mg/L as Cl_2 would have an expected steady state concentration of 0.95 mg/L as Cl_2 (Figure 4-15 A). A pH 9, a similar filter subjected to the same influent monochloramine concentrations would most likely exhibit steady state monochloramine concentrations around 1.2 mg/L as Cl_2 (Figure 4-15 B). The modeling efforts reflect the pH dependency seen in Phase 1 of the project. The higher pH (9 versus 8) causes a higher steady state monochloramine concentration.

When applying the MCAT model simulations, it is important to consider the quality of the fit of the calibrations presented in section 4.4.1. Looking at Figures 4-12 through 4-14, the MCAT model under-estimates the steady state monochloramine concentration at the 0.5 minute EBCT and over-estimates the concentration at the 1.5 minute EBCT. This result is similar to the results shown by Fairey et al. (2006) with the Centaur and AquaGuard GAC samples. In this previous research, the cause of the failure of the MCAT model to accurately capture the shape of the effluent profile was not determined. Fairey et al. (2006) noted that the rate expression used in the development of the MCAT model was based on F400 GAC sample; thus, manipulation of this rate expression could yield higher quality fits for these newer, “catalytic” activated carbons. Furthermore, it is possible that liquid film diffusion or surface diffusion is not negligible with the GAC samples considered in this research. The MCAT model neglects these mechanisms, and could justify the poorer fit of the experimental and modeling results. Regardless, the MCAT model predicts higher monochloramine concentrations and EBCTs of interest; thus, the modeling results serve as a conservative estimate of the

steady state values. In reality, the impact of other water quality parameters such as the concentration of natural organic matter are likely to have a greater impact on the predictions of performance than the differences between the data and model predictions shown here.

4.4.3. Feasibility for Full Scale Implementation

After obtaining results from the MCAT model simulations, it was possible to evaluate the suitability to point of use applications. The National Sanitation Foundation (NSF) independently tests and certifies water treatment systems for chloramine removal. In order for a particular point of use filter to earn "certification" for reduction of chloramines, it must be able to reduce chloramine from 3 mg/L as Cl_2 to 0.5 mg/L as Cl_2. Since this is the metric used to evaluate monochloramine removal in industry and residential applications, it was applied to determine the suitability of steady state monochloramine removal. Using the steady state effluent monochloramine concentration profiles presented in Figures 4-15 through 4-17, the EBCT that would be needed to produce a steady state effluent concentration of 0.5 mg/L with an influent concentration of 3 mg/L was determined at each pH valued tested. Results are presented in Table 4-11.

Table 4-11. EBCT required to meet NSF certification for monochloramine removal with steady state concentration determined from MCAT model simulations.

	EBCT (min)	
GAC	**pH 8**	**pH 9**
Jacobi CAT	2.05	2.60
Norit CAT	3.49	4.31
Norit CNS	4.54	5.39

The results suggest that for typical City of Austin tap water (pH of around 9.4 to 9.6 at the tap) nearly 3.0 minutes of empty bed contact time would be required to meet the NSF certification criteria using the top performing Jacobi CAT GAC. A little less than 5 and closer to 6 minutes of EBCT would be necessary if Norit CAT and Norit CNS were used, respectively. Aquasana is a manufacturer of various point of use filters. Their largest model of water filter can place GAC in a top and bottom tank. Using the dimensions specified by the manufacturer, the EBCT of this filter under typical operating conditions is exactly 2.0 minutes. Most of their other filters have EBCTs closer to 1 minute. This illustrates the feasibility of catalytic removal of monochloramine transcending real environmental engineering applications. Utilizing novel catalytic activated carbons, like Jacobi CAT, could lead to steady state operation using feasible empty bed contact times.

If 3.0 minutes of EBCT could produce a steady state monochloramine concentration meeting NSF criteria, the amount of time that a filter could run without replacing the media would be extended drastically. It would be interesting to compare if the benefit of utilizing the catalytic capability of the activated carbon by using a large filter would outweigh the upfront cost of purchasing extra media. In any instance, the simulation results prove very optimistic for incorporating steady state monochloramine catalysis into point of use drinking water filters.

The monochloramine standard for kidney dialysis water is 0.1 mg/L as Cl_2. Fairey et al. (2006) utilized the MCAT model to estimate the required EBCT to reach 0.1 mg/L as Cl_2 based on FBR results. Table 4-12 compares results from Fairey (2006) to those obtained by this study to reduce monochloramine from three different influent concentrations to 0.1 mg/L as Cl_2. This metric was determined from Kim's (1977) work

that found that impractically large EBCTs of between 25 and 35 minutes were required to reduce monochloramine to the kidney dialysis standard under steady state operation.

Table 4-12. EBCT required to meet kidney dialysis standard for monochloramine removal at pH 8 with steady state concentration determined from MCAT model simulations compared to results from Fairy (2006).

	EBCT needed to treat to 0.1 mg/L as Cl_2 (min)		
GAC	**1 mg/L Influent Conc.**	**2 mg/L Influent Conc.**	**3 mg/L Influent Conc.**
Jacobi CAT	4.09	5.18	5.42
Norit CAT	5.82	6.86	7.61
Norit CNS	6.25	8.20	8.86
F400	14.6	16.7	17.8
F600	10.5	13.6	14.6
Centaur	6.1	6.3	6.5
AGC-MG	13.6	16.7	17.8
AquaGuard	9.1	9.5	9.7

The results indicate that Jacobi CAT GAC required only between 4 and 5.5 minutes of EBCT to meet kidney dialysis standards utilizing catalytic removal. This surpasses the top performing carbon in Fairey's study, Centaur, which needed between 6 and 7 minutes of EBCT. Furthermore, it is clear that all three modified carbons tested in this study outperformed all other carbons tested in the previous study. However, it is important to consider that Fairey's research used Lake Austin Water, which could contain

20-40% more organic material, so it is impossible to claim that carbons tested in this research would outperform previously studied carbons using identical source water.

Since the tap water produced by the City of Austin has a pH of around 9, a similar analysis of empty bed contact times required to treat water to 0.1 mg/L as Cl_2 was performed. Results for the carbons tested in this research are summarized in Table 4-13.

Table 4-13. EBCT required to meet kidney dialysis standard for monochloramine removal at pH 9 with steady state concentration determined from MCAT model simulations.

	EBCT needed to treat to 0.1 mg/L as Cl_2 (min)		
GAC	**1 mg/L Influent Conc.**	**2 mg/L Influent Conc.**	**3 mg/L Influent Conc.**
Jacobi CAT	4.81	5.71	5.92
Norit CAT	6.18	8.01	8.64
Norit CNS	8.29	9.90	10.91

At the higher pH values, Jacobi CAT requires between 4.8 and 6 minutes of contact time to meet the needs of kidney dialysis. These results further justify the possible implementation of steady state monochloramine catalysis for real-world applications. While the empty bed contact time required for kidney dialysis is relatively high, the use of GAC is still feasible.

4.5. SUMMARY

The results of this research project were presented in three phases. In Phase 1, monochloramine destruction was quantified based on source water type and GAC identity by implementing laboratory scale FBR studies. The results confirmed previous

research, and indicated that a steady state effluent concentration was reached after a period of higher removal. At both pH values considered (8 and 9), the performance of the activated carbons could be ranked as follows, with number 1 indicating the highest removal: (1) Jacobi CAT, (2) Norit CAT, and (3) Norit CNS. The results showed that monochloramine removal decreased with increasing pH, to varying degrees based on the GAC type. Removal efficiency was larger at pH 8 than pH 9 for all GACs test considered. This could be a result of monochloramine stability and the nature of GAC surface oxides.

In Phase 2, the physical and chemical characteristics of the GACs used in Phase 1 were evaluated. Physical characterizations were performed using various analyses of nitrogen gas adsorption isotherms at 77 K. Results showed that Jacobi CAT was highly microporous, suggesting that the size exclusion of natural organic matter greatly impacted monochloramine catalysis, in a positive manner. Both Jacobi CAT and Norit CAT had very similar specific surface areas, while Norit CNS was significantly lower. The acid/base character of each activated carbon was quantified using Boehm titration methods. Norit CNS exhibited the most unfavorable acid/base character, and also performed the worst. However, Norit CAT had the most favorable chemical characteristics, slightly better than Jacobi CAT. These results suggest that the physical pore distribution impacts on NOM are more significant than pure chemical characteristics.

The chemical composition of the surface of each GAC was qualitatively described using FTIR analysis. Quinones, Lactams, Imides, and lactones were shown to exist as surface function groups on each carbon. Lactones have been shown to reduce monochloramine in previous studies. Furthermore, Imides have pKa's between 8 and 10, which could provide insight into the pH decency of monochloramine reactions. Statistical

correlations were used to support experimental findings to determine the physical and chemical properties that most influenced removal. Increased micropore volume showed a significant correlation with steady state performance.

Finally, Phase 3 utilized results from the first two phases to calibrate the MCAT model of Kim (1977). The model provided a reasonable but conservative estimate of steady state monochloramine concentrations. After running simulations of full scale point of use applications, it was found that approximately 3.0 minutes of EBCT should be sufficient to meet the NSF monochloramine removal certification criteria. These results could be used to implement monochloramine-GAC catalysis into real-world point of use applications. Furthermore, the MCAT model was used to predict contact times necessary to meet the kidney dialysis standards of 0.1 mg/L as Cl_2. It was found that between 4 and 6 minutes were necessary for the Jacobi CAT carbon, while between 6 and 11 minutes were necessary for the other two carbons tested. Results were compared to carbons tested in a previous study (Fairey et al., 2006) and showed that the Jacobi CAT carbon compared favorably to other catalytic carbons. However, the impact of organic matter on removal is a key factor that must be considered further.

Chapter 5: Conclusions

5.1. Overview of Research

The objective of this project was to investigate the catalytic reduction of monochloramine using granular activated carbon, with regard to implementation in point of use filters. Previous work in the 1980's has shown that a catalytic process does occur. In 2006, Fairey et al. studied several new catalytic GACs. This work showed that modified activated carbons can destroy monochloramine more efficiently than non-modified samples. The point of use drinking water filter has been incorporated into many households. No previous research exists investigating the feasibility of steady state monochloramine catalysis in point of use applications. This research was intended to bridge this gap.

The goals of this research were threefold. First, steady state monochloramine reduction would be quantified using fixed bed reactor studies. Next, the physical and chemical GAC properties would be determined and compared to FBR results. These results would be used to further tailor optimum GAC parameters for monochloramine removal. Finally, the implementation of monochloramine catalysis into point of use drinking water filters would be investigated. The research was divided into three phases to accomplish the research goals.

1. A laboratory scale fixed bed reactor experiment was used to quantify steady state monochloramine removal over time. City of Austin tap water was used for three GAC types (Jacobi CAT, Norit CAT, Nority CNS) at pH 8 and 9.
2. Physical characterization of each GAC was performed using analysis of nitrogen adsorption isotherms. Specific surface area, pore volume, and pore distribution was determined. Chemical characterization was

performed quantitatively using acid/base uptake Boehm titrations. Qualitative analysis was performed by analyzing FTIR spectra.

3. The MCAT model was calibrated using results from the Phase 1 and 2. Simulations of full scale point of use drinking water filters were run for various EBCTs and influent monochloramine concentrations. These results were compared against NSF monochloramine reduction criteria.

5.2. CONCLUSIONS

Major conclusions from each of the three phases of this research are outlined and presented below:

- Monochloramine effluent concentrations from the FBR studies reached steady state values after a period of higher removal. These steady state values are dependent on empty bed contact time, GAC characteristics, and influent water characteristics.
    - This supports previous claims that monochloramine removal with granular activated carbon is a catalytic process.
- Jacobi CAT proved far superior than all other GACs tested in the FBR studies, based on steady state removal efficiency, for each condition tested. The ranking of GACs tested, starting with the highest steady state monochloramine removal is: Jacobi CAT, Norit CAT, Norit CNS.
    - At the laboratory scale, nearly 90% monochloramine removal can be achieved using Jacobi CAT at a 0.75-minute EBCT.
- Removal efficiency decreased with increasing pH in FBR studies. This could be a result of increased monochloramine stability based on

monochloramine chemistry. Also, functional group dissociation constants could further explain pH dependencies shown experimentally.

- Some trends in acidity and basicity of the GACs were shown; however, surface chemistry of the GAC was not shown to be the most significant feature contributing the removal.
    - Norit CNS had the least ideal surface chemistry, and also performed the worst in the FBR studies.
    - However, Norit CAT had the most ideal surface chemistry, but did not perform the best.
- Lactones, Lactams, Imides, and Quinones shown during FTIR spectroscopy at different intensities. These functional groups are likely involved in monochloramine catalysis reactions.
    - Lactones have been shown to reduce monochloramine.
    - Imides have pKa's within the operating range of point of use filters (8-10); this further accounts for pH dependencies of reactions.
- Jacobi CAT's physical analysis demonstrates a highly microporous structure. Previous research has shown that NOM cannot penetrate these micropores. This size exclusion could mean that most of the active sites in a microporous GAC are free to proceed with monochloramine catalysis. This could provide insight into Jacobi CAT's superior removal of monochloramine.
- Size exclusion due to pore size distribution (physical characteristic) seems to overwhelm the impact of acidity/ basicity and surface chemistry.
- Significant correlations between steady state monochloramine removal efficiency and micropore volume were shown. This was described by

calculating the coefficient of determination (R^2) of the linear regression between each physical/chemical property and steady state removal.

  - Increased micropore volume proved to correlate with performance.
  - Total BET surface area, total pore volume, and basicity of the GACs tested failed to show significant correlations with performance. Acidity values were statistically identical.

- The MCAT model provides a basis for estimating the steady state removal in full scale point of use applications.
  - The model can be calibrated for a variety of GACs, pH values, and influent source water characteristics.
  - Based on the calibration fits, it provides a somewhat conservative simulation of steady state performance.
- Research results with the MCAT model simulations predict between 2.5 and 3.0 minutes of EBCT would be necessary to provide a steady state effluent monochloramine concentration that meets NSF certification criteria.
  - Since present filters provide around 1.0 to 2.0 minutes of EBCT, the use of monochloramine catalysis in full scale applications seems feasible.
- At a pH of 9, Jacobi CAT requires between 4.8 and 6 minutes of contact time to meet the needs of kidney dialysis.
  - This is a larger EBCT than usually used in filters; however, it could still be feasible.

- Experimental results and modeling efforts further justify the possible implementation of steady state monochloramine catalysis for real-world applications.

5.3. SIGNIFICANCE

This work analyzed three activated carbons that have been recently developed and are currently implemented in point of use filters. The results can be used to tailor future activated carbons to perform more efficiently in terms of steady state monochloramine removal. The importance of physical and chemical properties of GACs was elucidated in this research. Surface chemistry is obviously an important aspect that controls the rate of the monochloramine-GAC reactions. However, in any natural water containing significant amounts of organics, the size exclusion phenomenon exhibited with micropores outweighs chemistry. If the FBR studies in this research were performed in organic-free water, results could demonstrate that Norit CAT could outperform the Jacobi CAT, based on a more favorable surface chemistry.

This point brings another significant outcome of this research: The monochloramine catalysis with GAC is not only dependent on the GAC properties, but the influent source water characteristics. Organic matter concentrations and types, and pH clearly influence the steady state reduction of monochloramine. When tailoring a GAC to remove monochloramine, it is also imperative to perform an analysis on the influent water. Tap water characteristics vary significantly throughout various regions.

Of most significance in this research is the ability to apply this work into full scale point of use filtration devices. Results show that 2.5 to 3.0 minutes of EBCT could provide steady state effluent concentrations meeting NSF criteria for monochloramine

removal certification. The steady state operation of a GAC point of use filter means that monochloramine could be removed for extended periods of time to the steady state concentration. Thus, it would be interesting to see if the drastically extended filter run times could make up for the cost of providing larger empty bed contact times. Larger EBCTs were required to meet the needs of kidney dialysis. The feasibility of monochloramine catalysis in this application requires further analysis, and is within the range of possibility.

5.4. FUTURE WORK

Although this research provides insight into the application of monochloramine-GAC catalysis into point of use filters, several aspects warrant further investigation. Highlighted below are several recommendations for future work.

- Utilize Raman spectroscopy and XPS spectroscopy on GAC samples to gain further insight on the chemical aspects of the surface functional groups.
- Perform FBR studies using various influent source water types with varying degrees of natural organic matter. It would be interesting to fully understand the performance of each activated carbon with regards to organics. It is possible that certain carbons would perform better than others as NOM varied, meaning point of use filtration manufacturers could further tailor their filters by source water characteristics.
- Apply $SUVA_{254}$ analysis of the organics considered in FBR studies to characterize source water organics by type, rather than just organic carbon concentration.

- Perform full scale testing using US 12 X 40 mesh size to confirm the MCAT model's prediction of EBCT required to achieve a steady state effluent monochloramine concentration meeting NSF's criteria.
    - Run this full scale test for long periods of time to see if the steady state catalytic capacity is ever reached and steady state removal is no longer seen. Previous studies have run experiments for long periods of time and have not seen an end to steady state. However, full scale application requires a clear capacity, so it is necessary to determine if and when catalysis ends.
- Use results from these studies to design a filter that can apply monochloramine-GAC catalysis to destroy monochloramine.
- Complete a cost/benefit analysis to determine if this product could out-compete filters currently on the market by providing greatly prolonged filter run times without the need for replacement.

Appendix A: Data from the FBR Studies

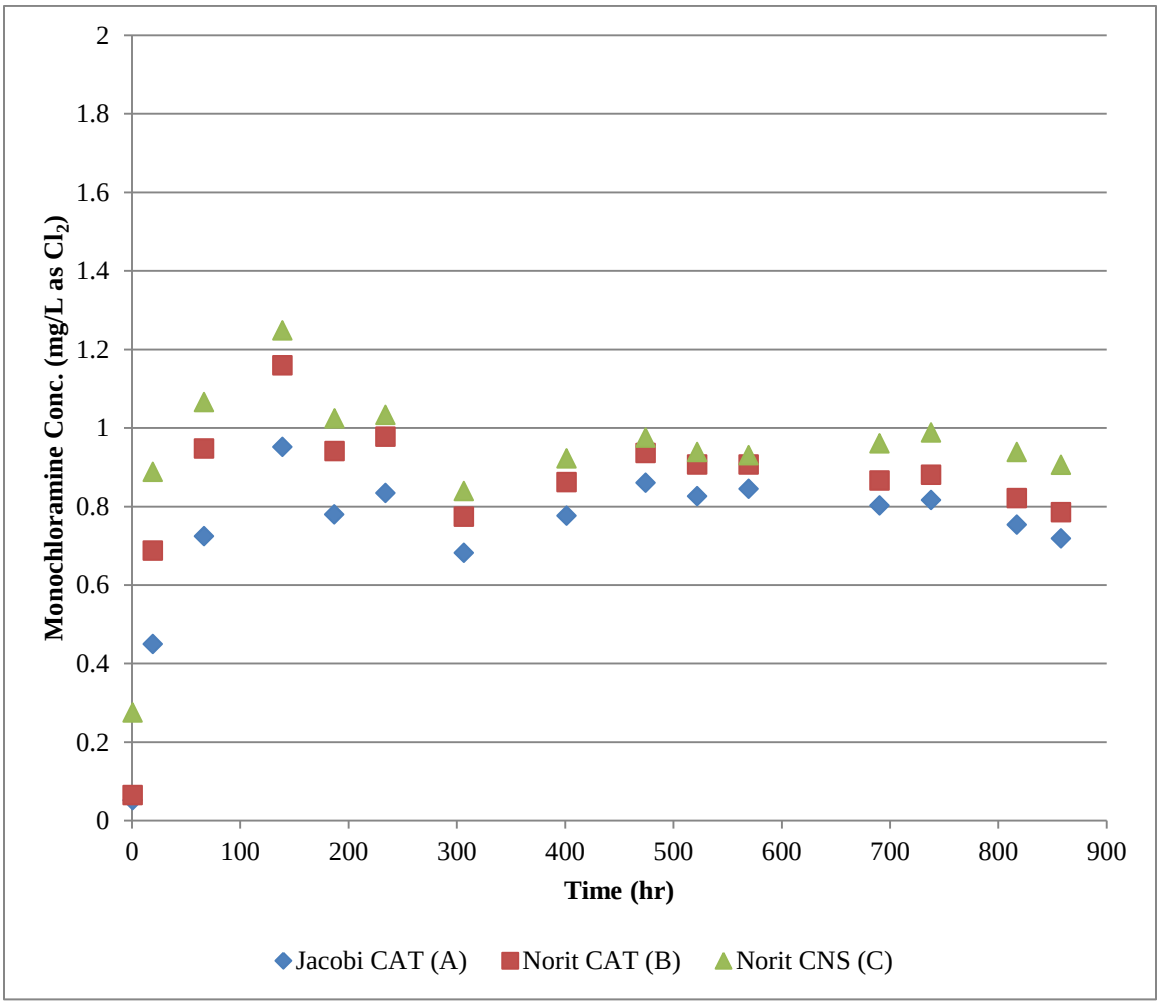


Figure A-1. Monochloramine concentration versus time for 0.25 minute EBCT.

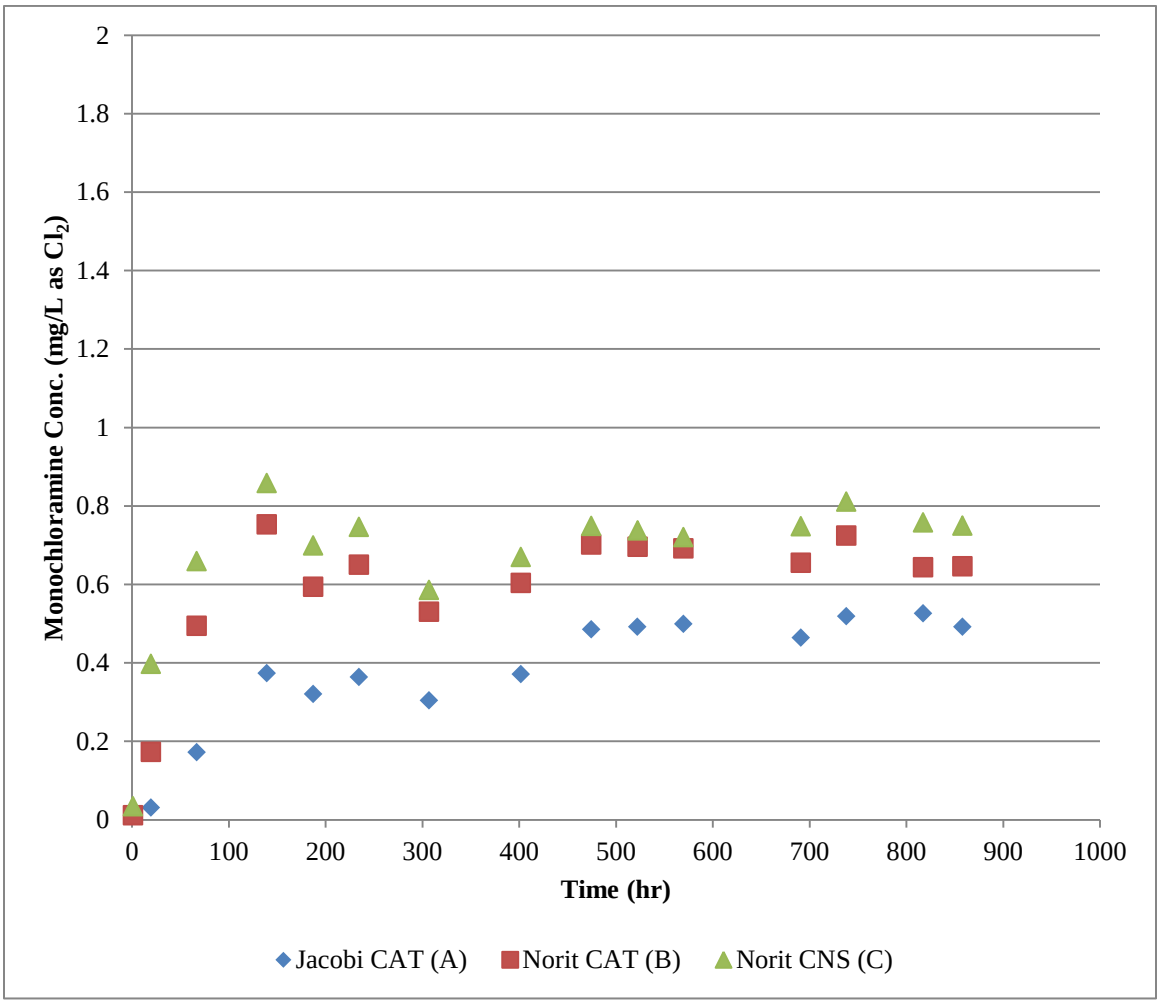


Figure A-2. Monochloramine concentration versus time for 0.5 minute EBCT.

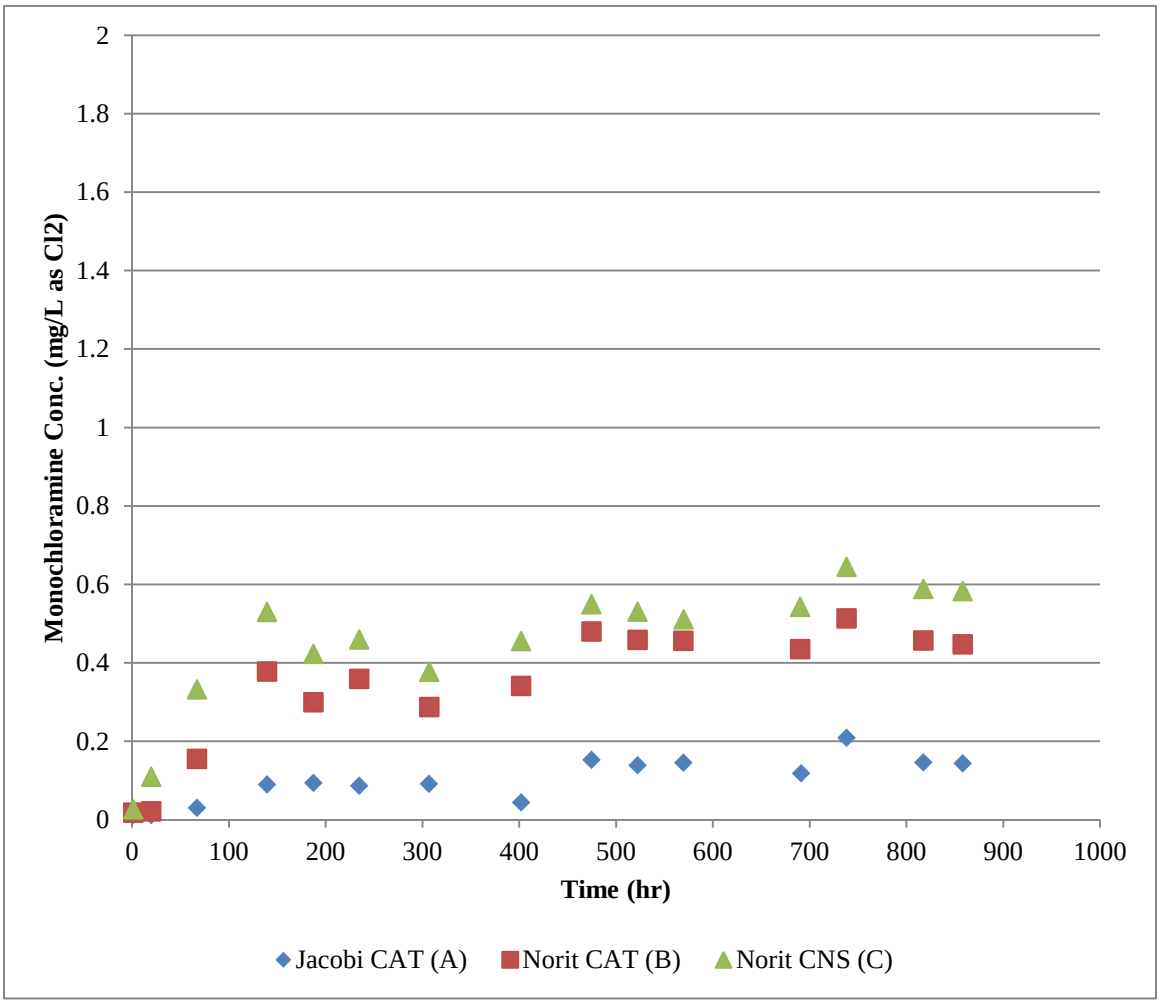


Figure A-3. Monochloramine concentration versus time for 0.75 minute EBCT.

Appendix B: Physical Characterization of GACs with Nitrogen Gas Adsorption Isotherms

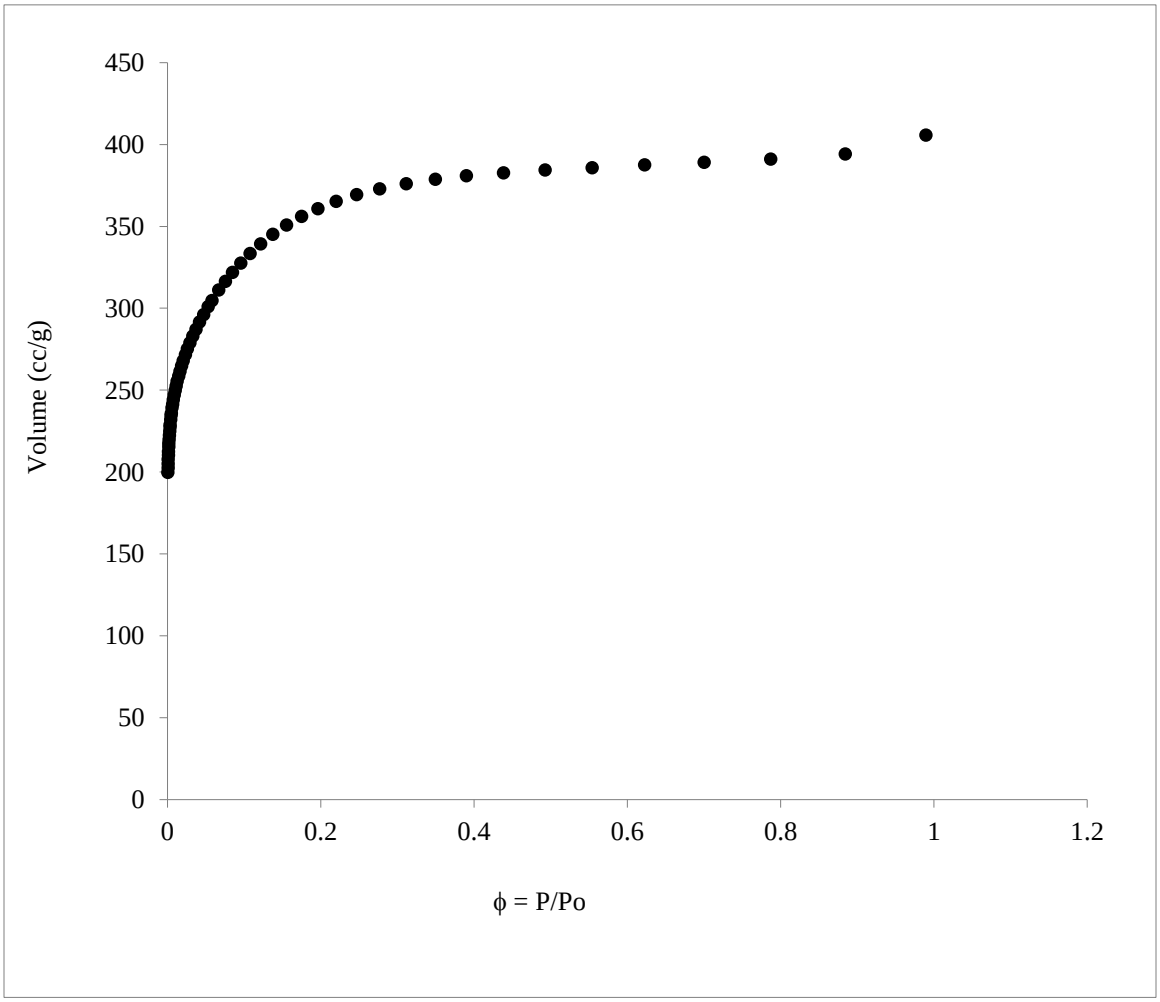


Figure B-1. Nitrogen gas adsorption isotherm for Norit CAT.

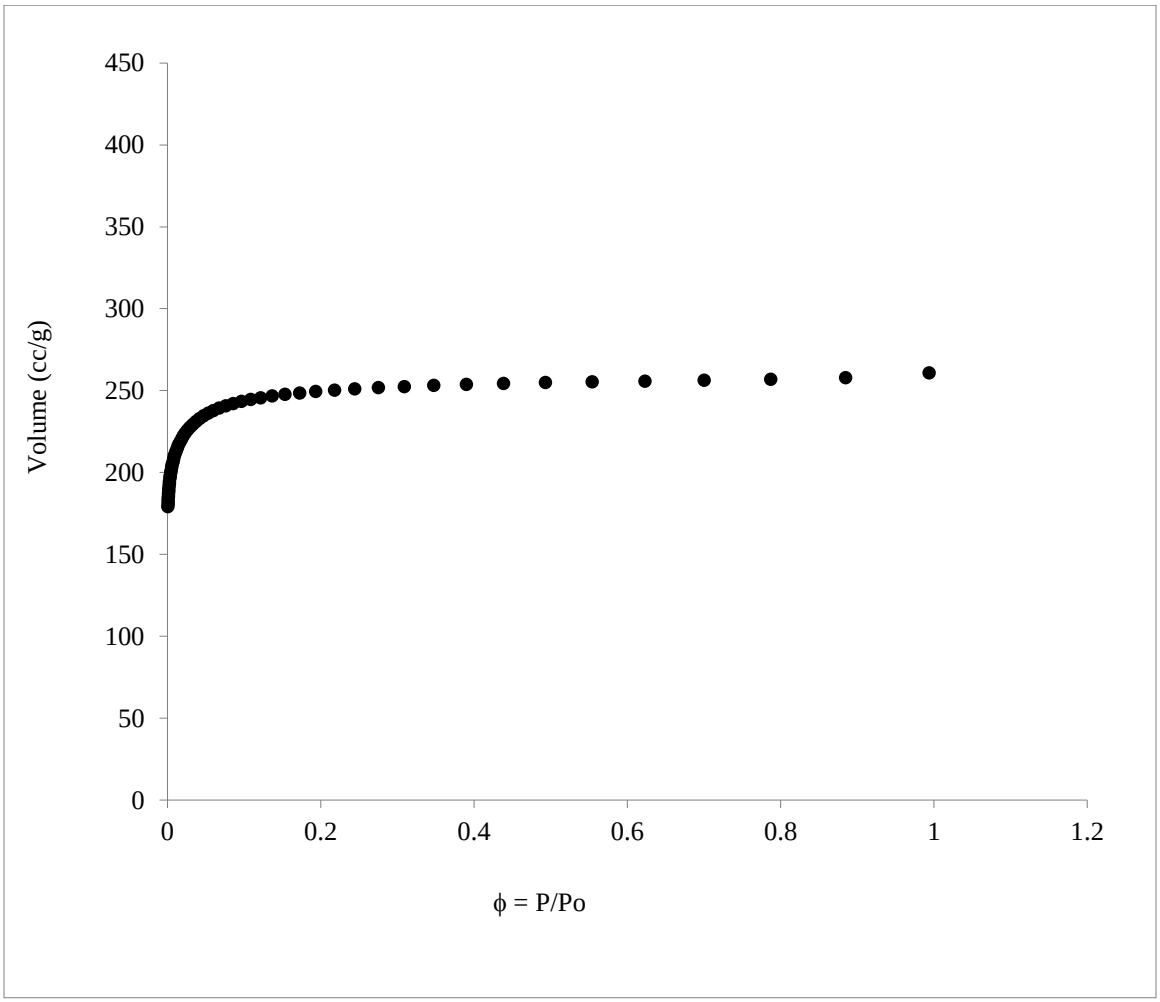


Figure B-2. Nitrogen gas adsorption isotherm for Norit CNS.

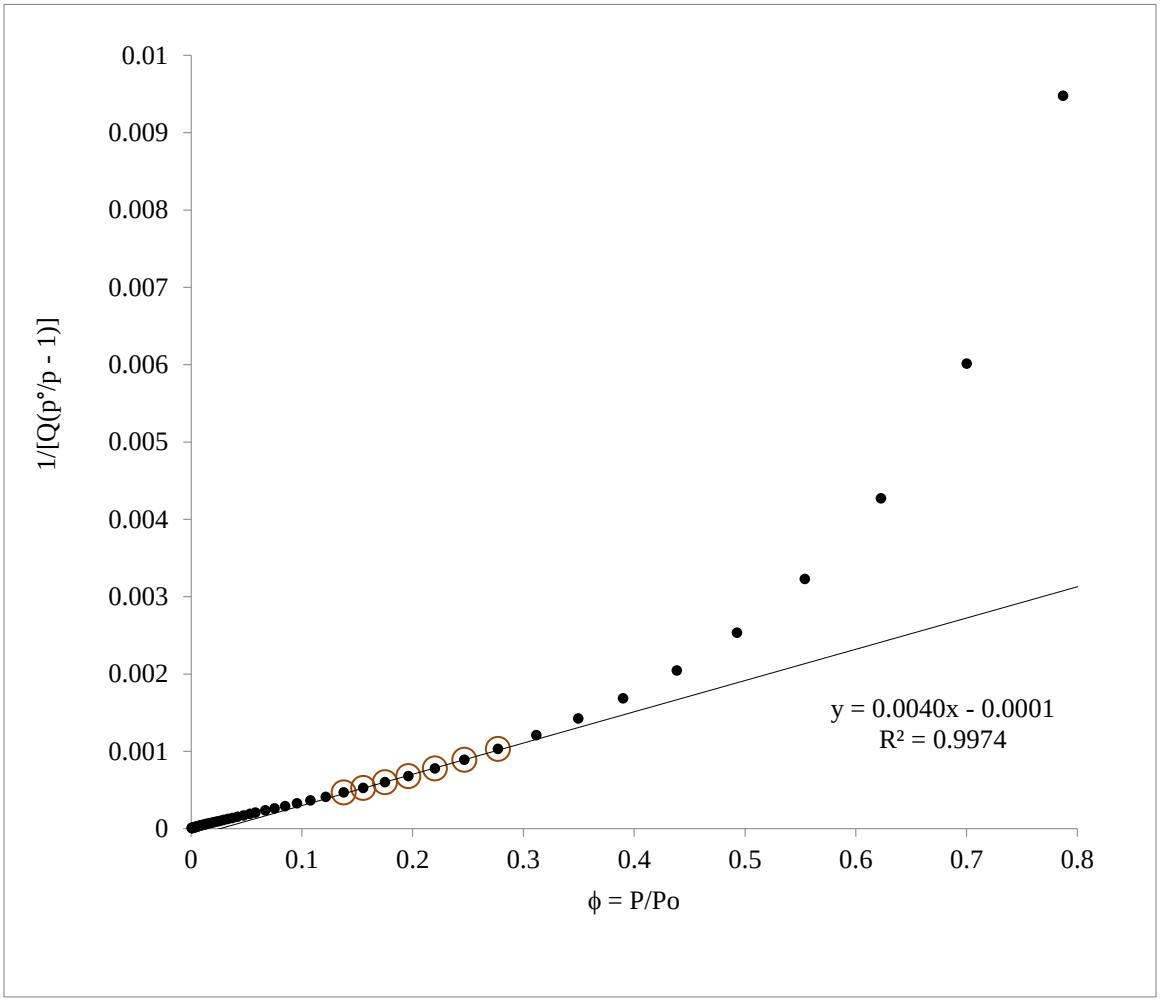


Figure B-3. BET plot for Norit CAT.

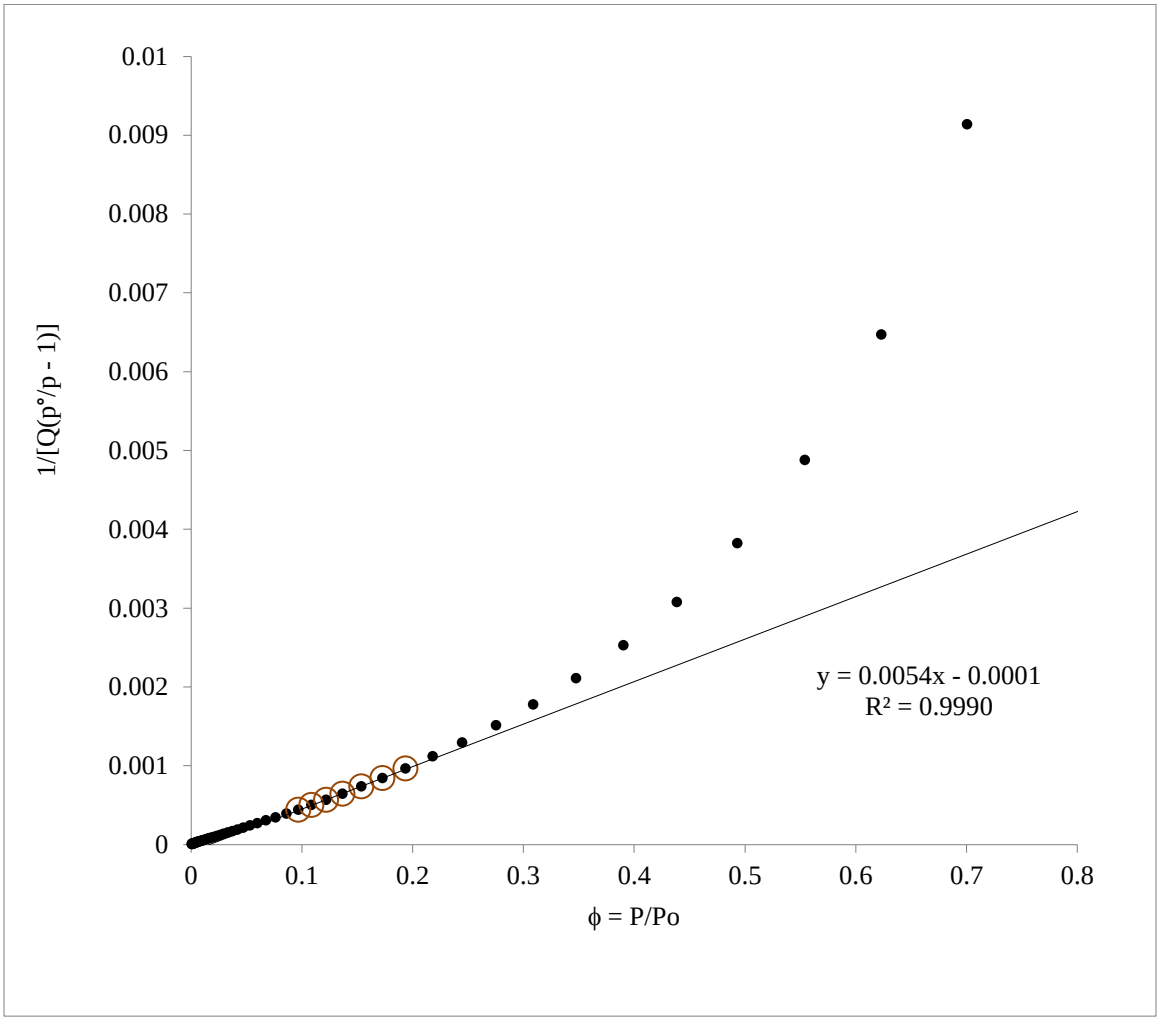


Figure B-4. BET plot for Norit CNS.

Appendix C: Chemical Characterization Data

C.1. Boehm Titration Data

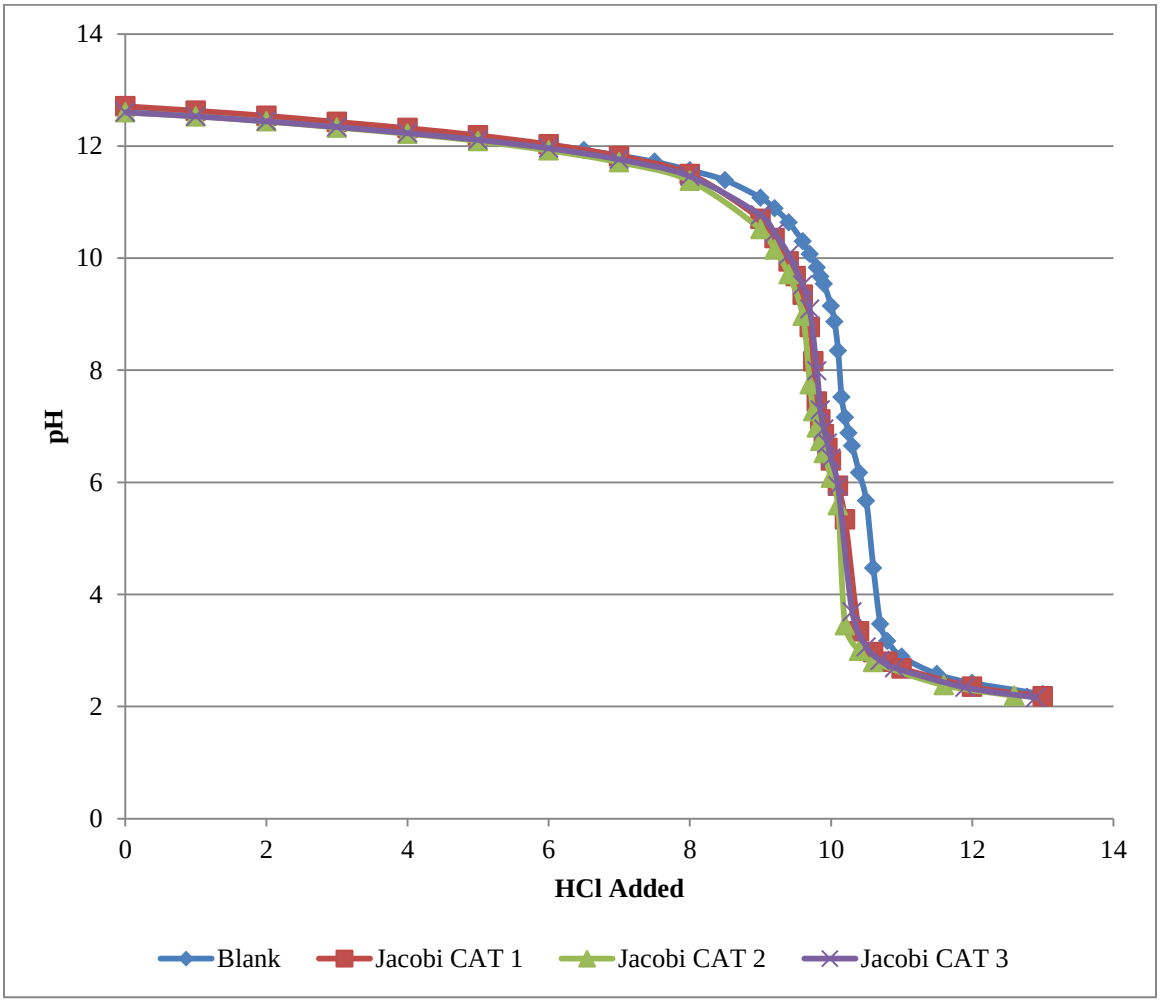


Figure C-1. NaOH uptake titration curve for Jacobi CAT to determine total acidity.

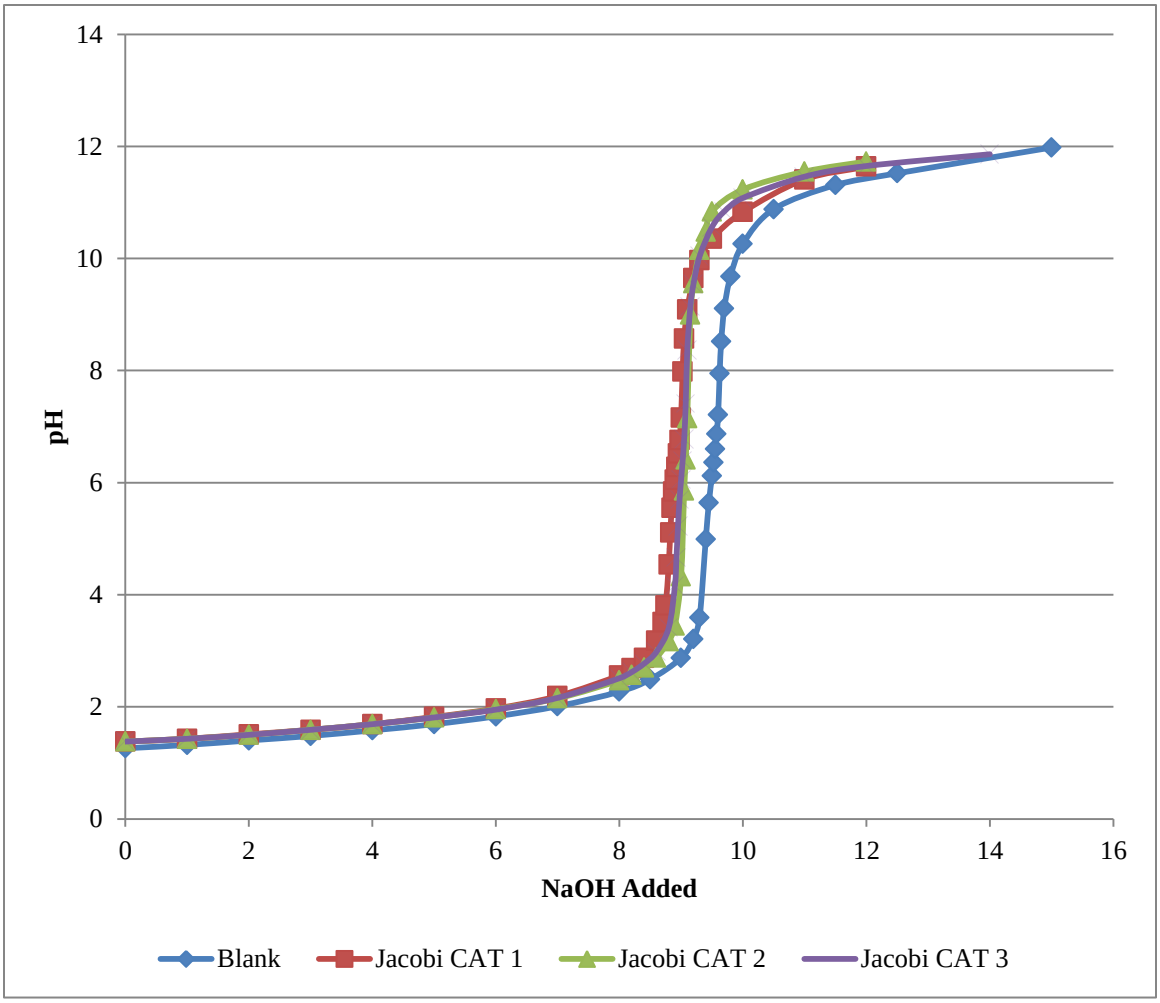


Figure C-2. HCl uptake titration curve for Jacobi CAT to determine total basicity.

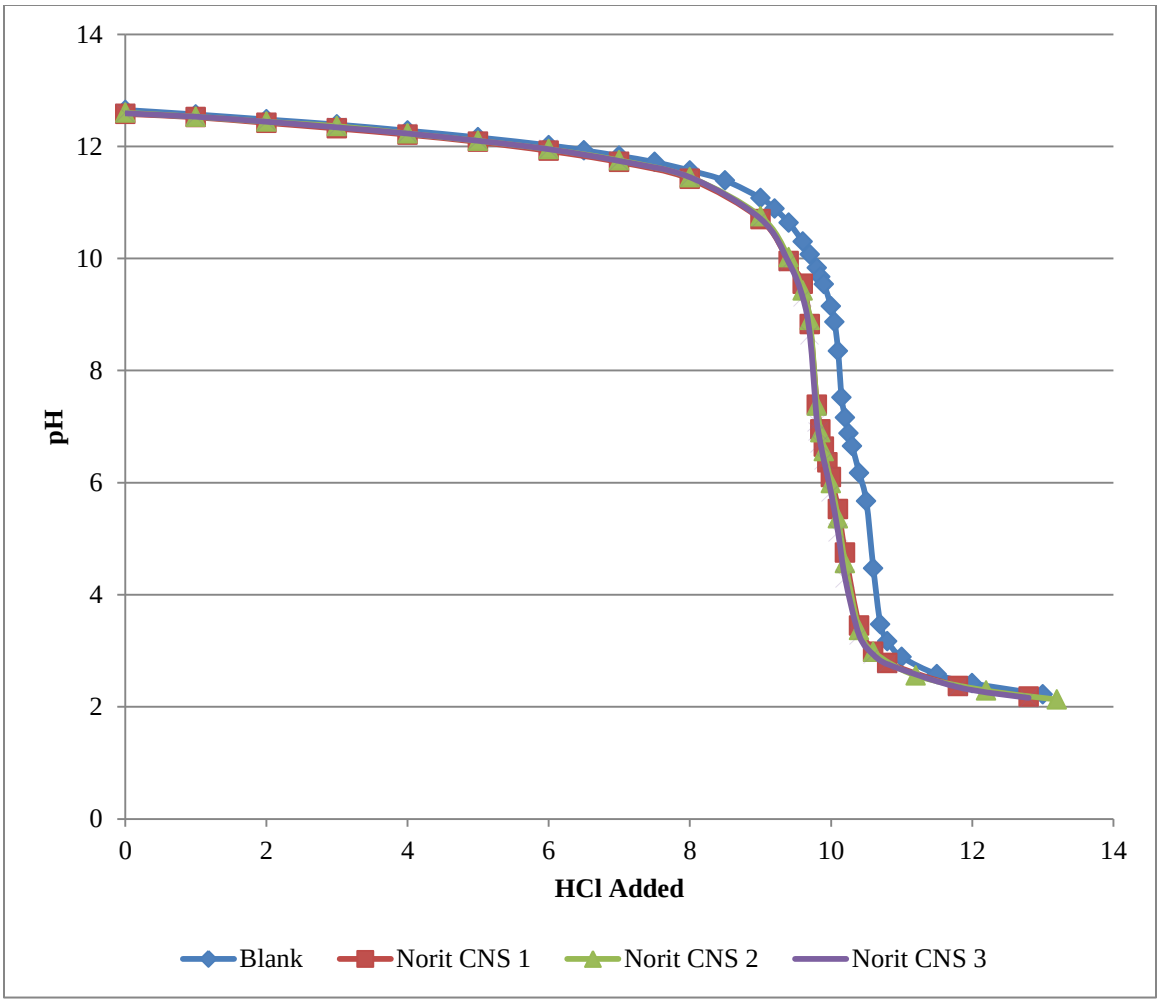


Figure C-3. NaOH uptake titration curve for Norit CNS to determine total acidity

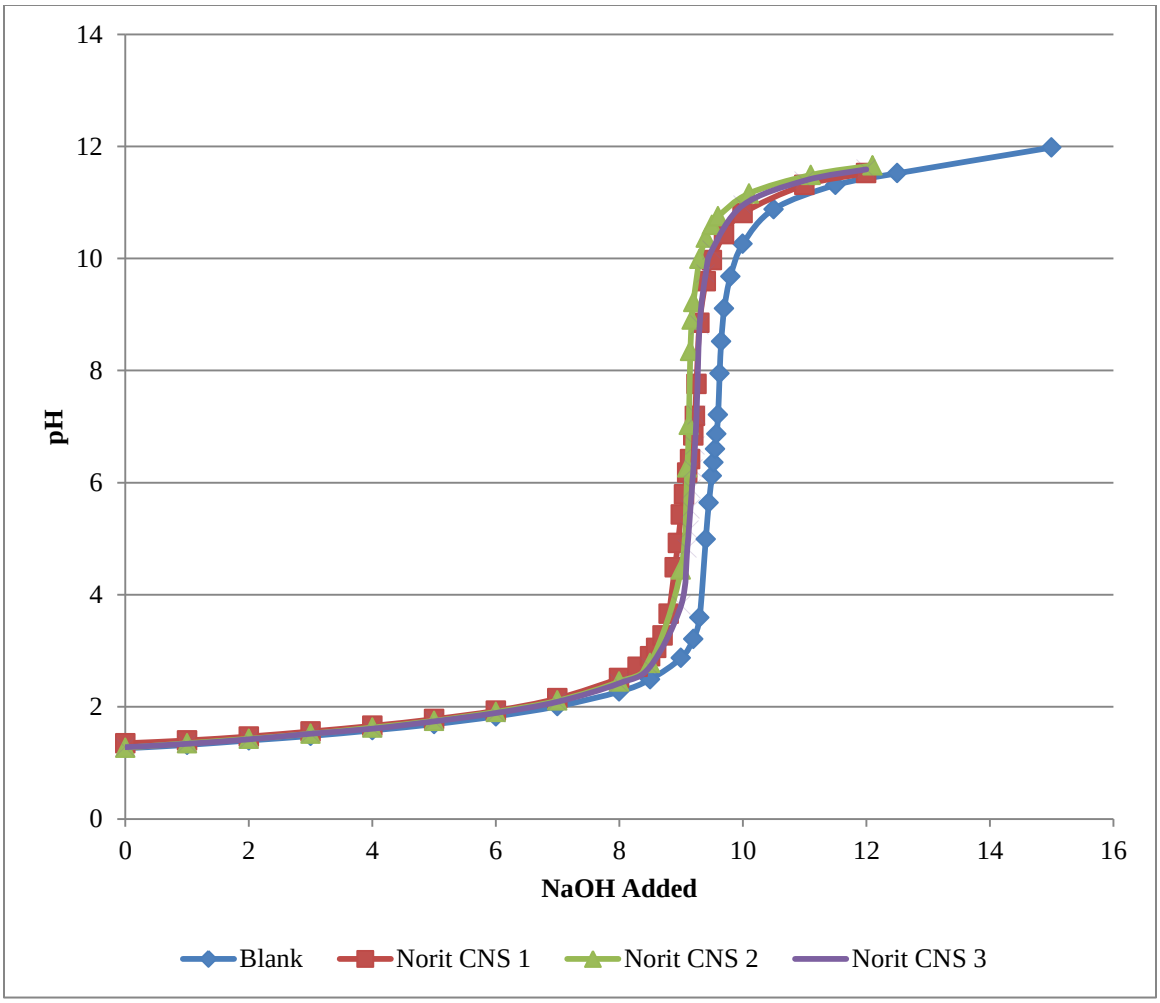


Figure C-4. HCl uptake titration curve for Norit CNS to determine total basicity.

C.2. FTIR SPECTROSCOPY

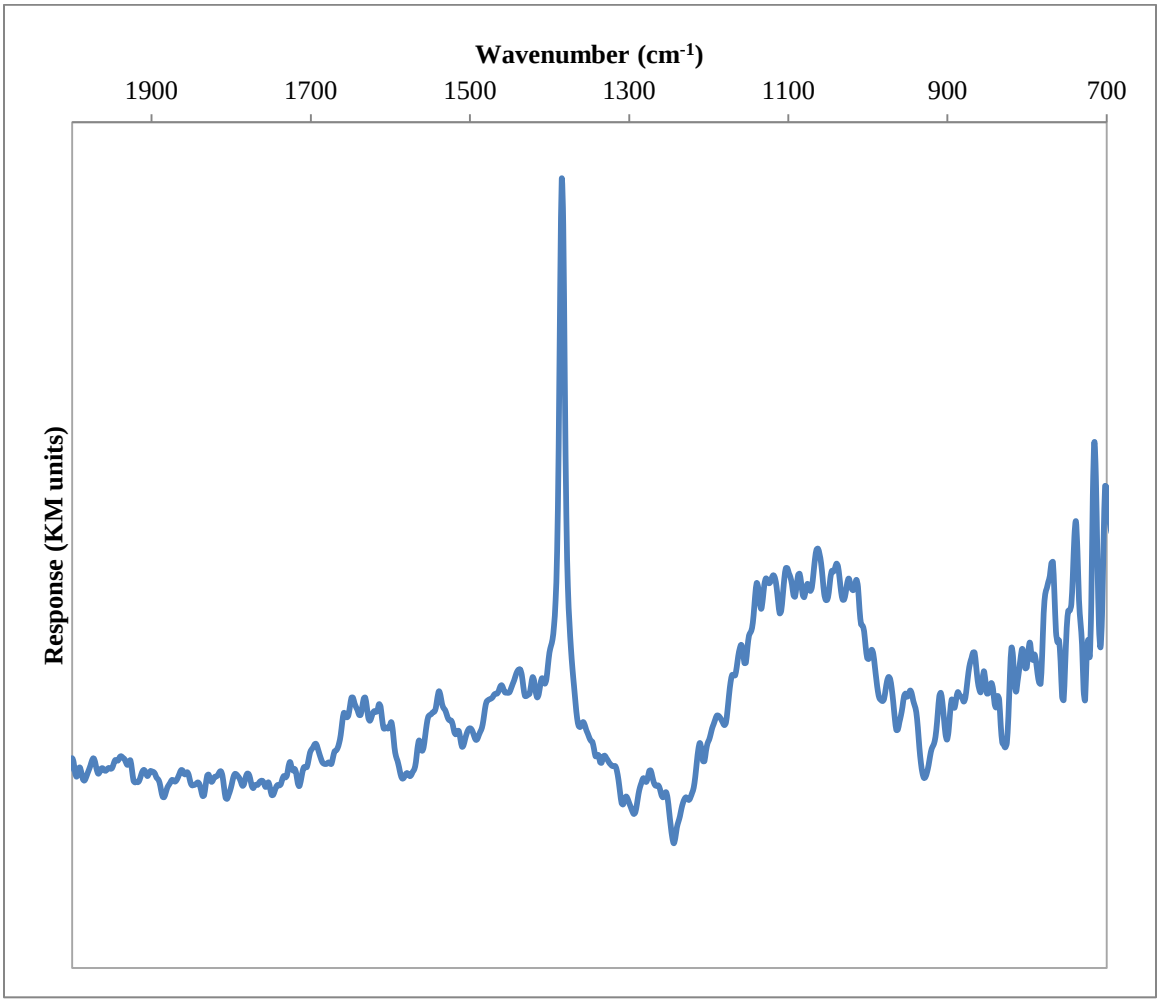


Figure C-5. FTIR spectra for Jacobi CAT.

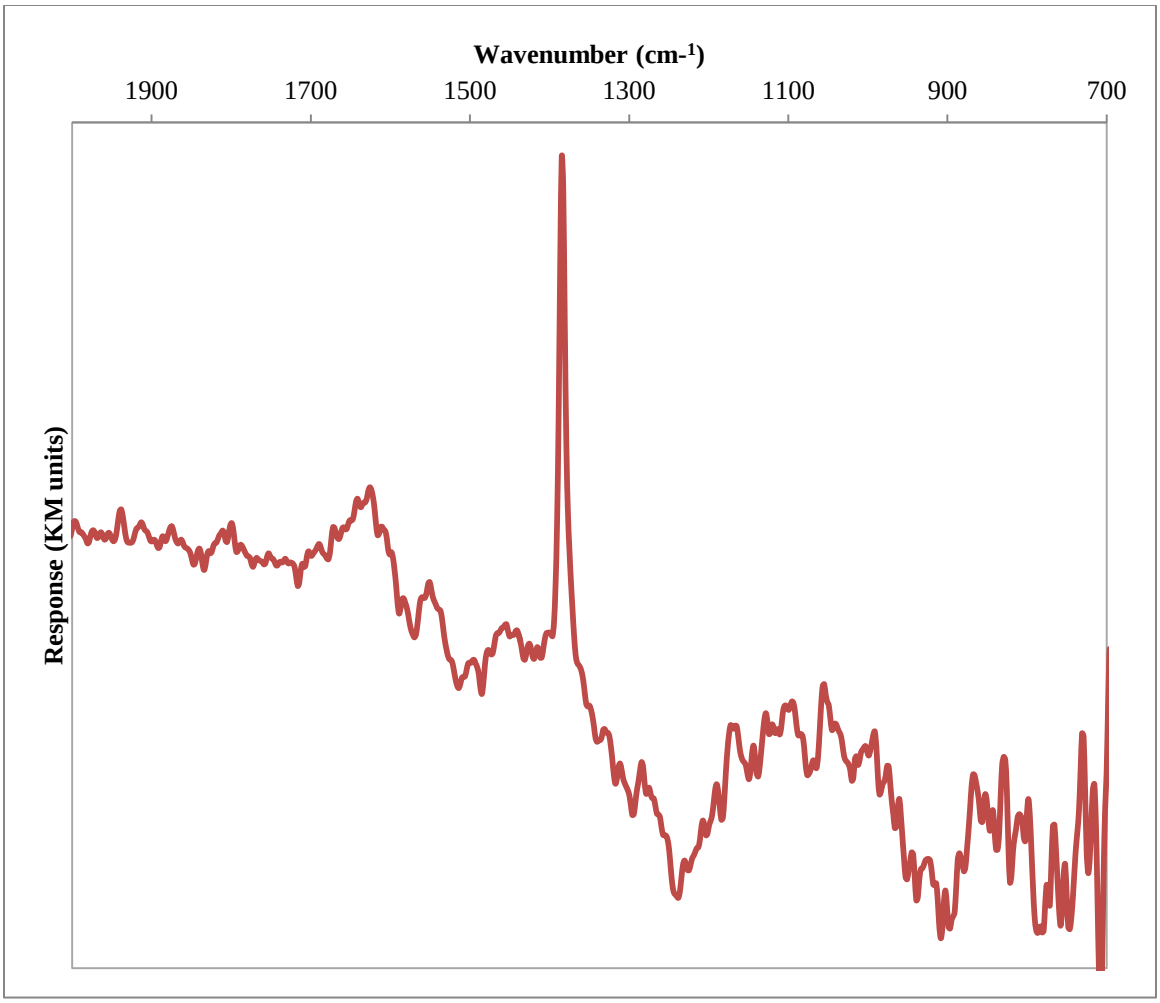


Figure C-6. FTIR spectra for Norit CAT.

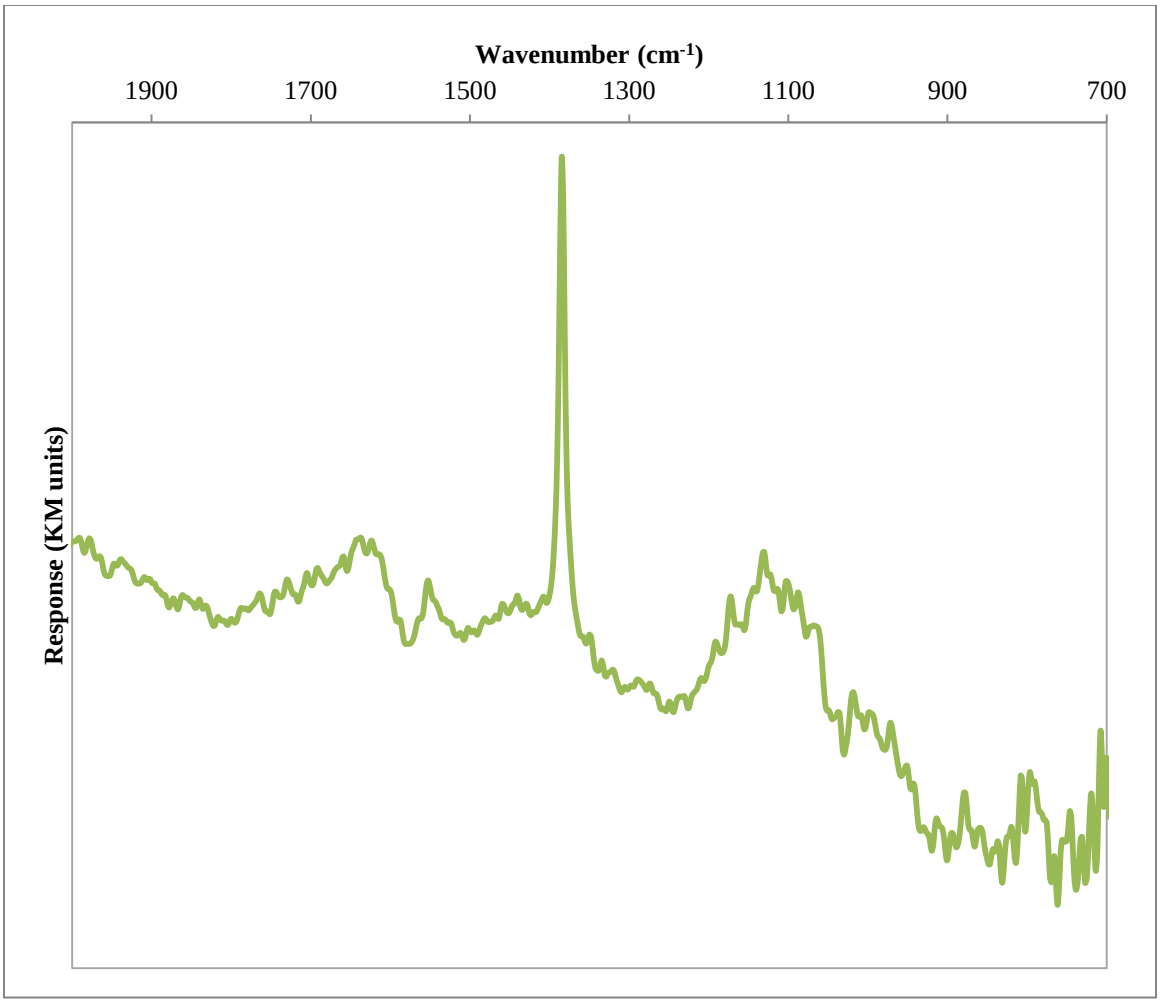


Figure C-7. FTIR spectra for Norit CNS.

Appendix D: Figures to Determine Correlations Between Physical/Chemical Properties and Steady State Performance

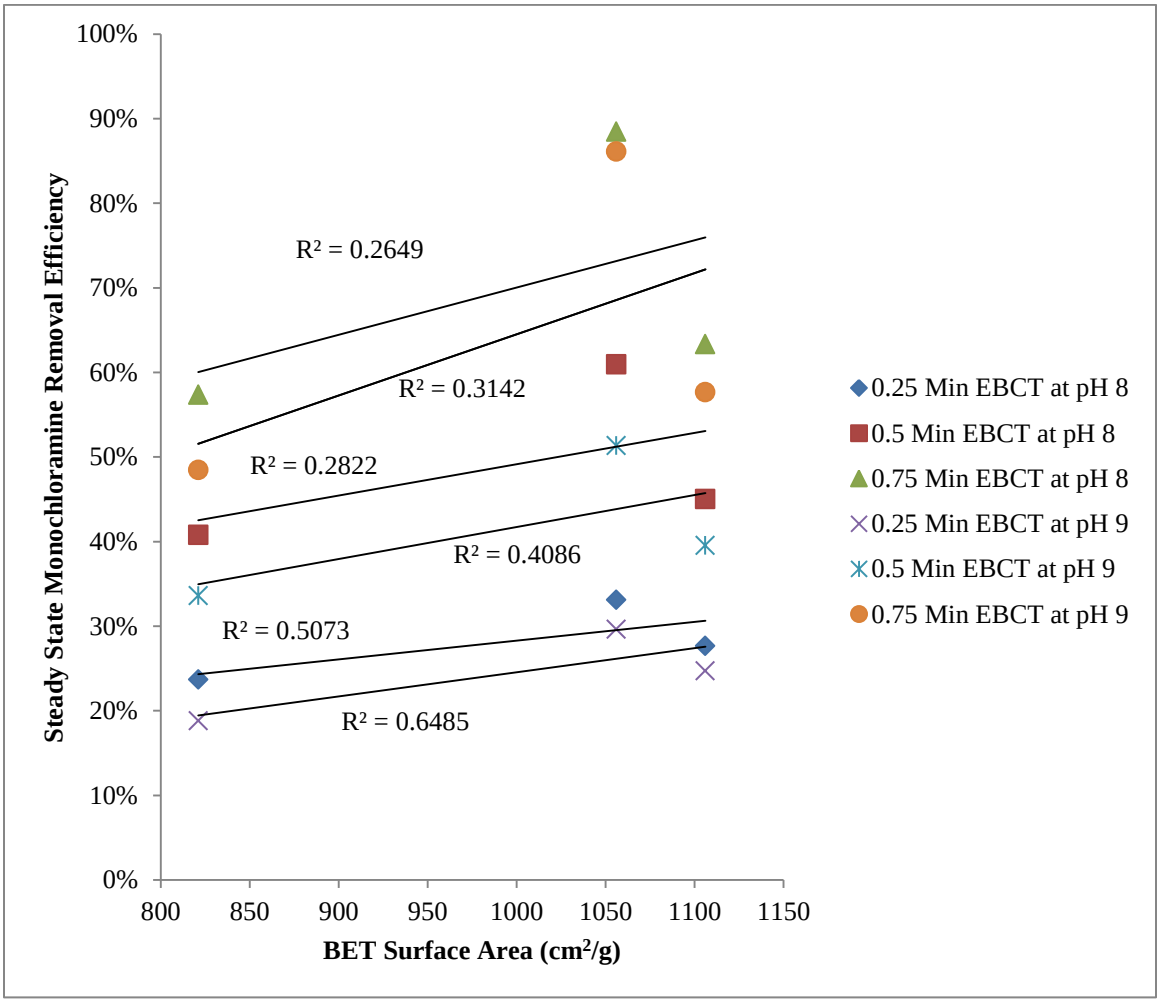


Figure D-1. Steady state monochloramine removal efficiency versus BET surface area.

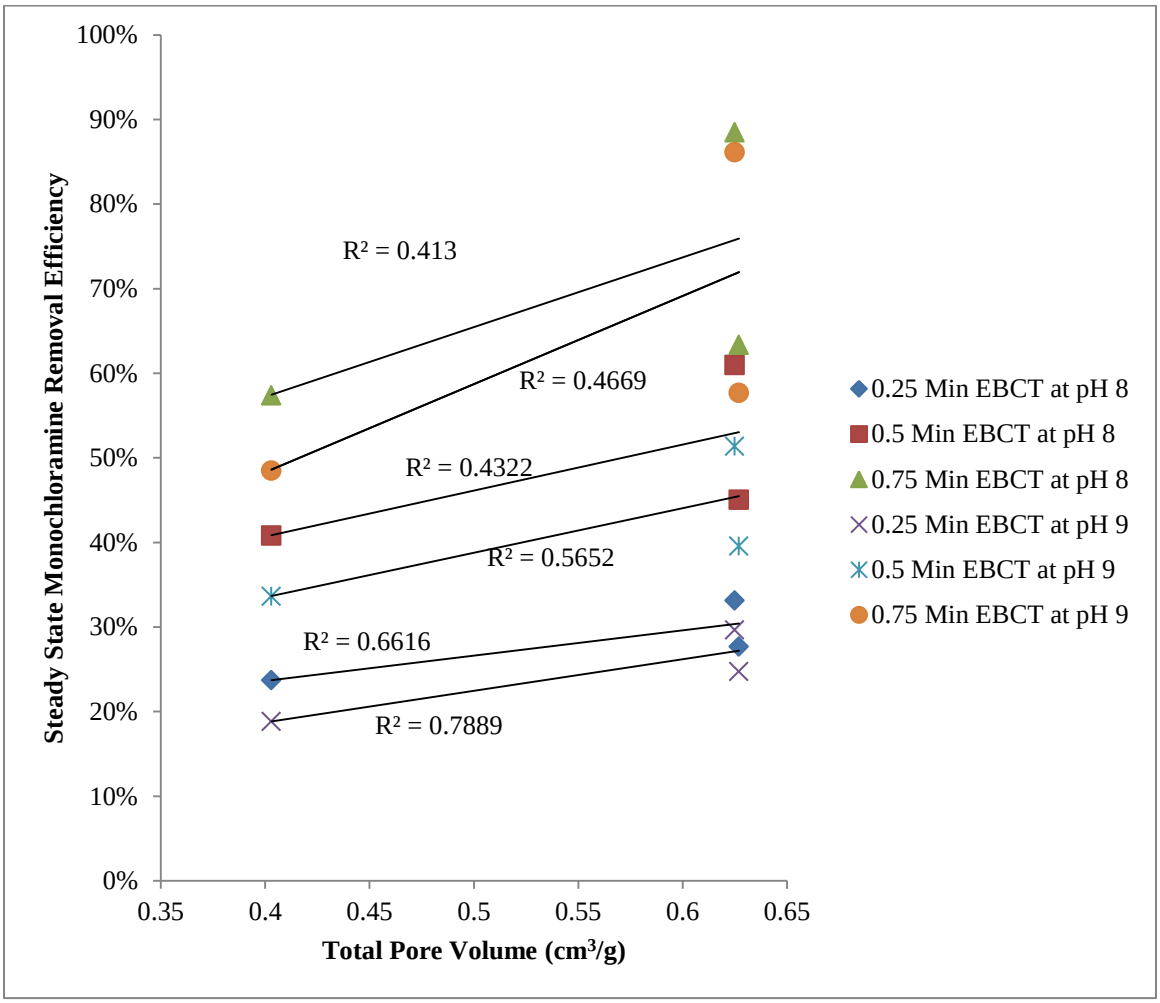


Figure D-2. Steady state monochloramine removal efficiency versus total pore volume.

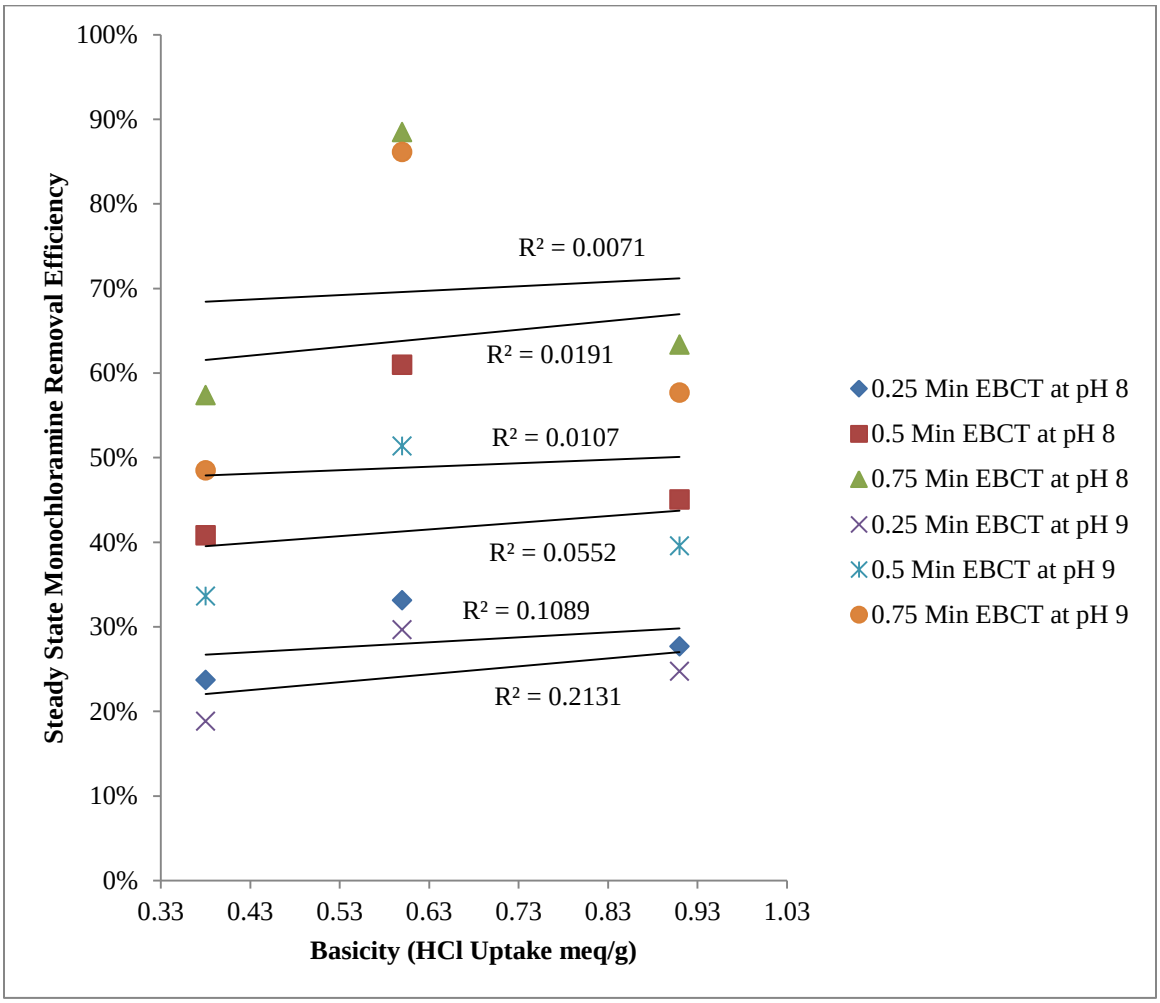


Figure D-3. Steady state monochloramine removal efficiency versus basicity measured as HCl uptake.

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Vita

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